

## Synthesis of Dialkyl-substituted Terminal Olefin

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**Abstract:** Dialkyl-substituted terminal olefins were synthesized from the coupling reaction of  $\alpha$ -olefins which were catalyzed by zirconocene dichloride/methylalumoxane (MAO) catalyst system under mild condition. High yield was gained and no other oligmer was detected. It was found that the ratio of Al/Zr is responsible for the selectivity of product.

**Keywords:** Zirconocene dichloride, methylalumoxane, dialkyl-substituted terminal olefin, coupling reaction.

Olefin is a sort of very important unsaturated aliphatic hydrocarbon. It can be used for synthesizing halide<sup>1</sup>, epoxide<sup>2</sup>, resin, ether and other olefin derivatives<sup>3</sup>. Moreover, it has a significant role to play as additive in dope, dye and petroleum that are indispensable to human being<sup>4</sup>. However, the familiar olefin is interval olefin or monosubstituted terminal olefin, and dialkyl-substituted terminal olefin **2** (**Scheme 1**) has rarely been reported. The reaction of aromatic or aliphatic C-H bonds with terminal alkynes can give dialkyl-substituted terminal ethenes, when it was photocatalyzed by  $\text{RhCl}(\text{CO})[\text{P}(\text{CH}_3)_3]_2$  under mild conditions, but the performance of activation is poor<sup>5</sup>. Vinyltrialkylborates derived from trialkylboranes and trisilylhydrazones of methyl ketones by treatment with iodine, 1,1-dialkylethenes also can be prepared<sup>6</sup>. The cross-coupling reaction of organozinc chlorides with (*Z*)-2-bromo-1-alkenylboranes proceeds in the presence of a palladium catalyst to give 2,2-disubstituted alkenylboranes, which can be used for synthesis of the disubstituted alkene<sup>7</sup>. But this method is too complicated to be industrialized, also the toxicant can threaten environment.

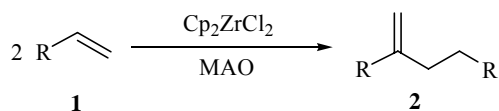
In this paper, we report the straightforward synthesis of dialkyl-substituted terminal olefins from the coupling reaction of  $\alpha$ -olefins catalyzed by zirconocene dichloride/MAO catalyst system under facile conditions (**Scheme 1**). This method afforded good yield and high selectivity for dialkyl-substituted terminal olefin. The high selectivity of product was dependent on the amount of co-catalyst MAO.

### Experimental

All reactions involving air- or moisture- sensitive organometallic reagents were carried

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**Scheme 1** Synthesis of dialkyl-substituted terminal olefin

out under dry nitrogen. Toluene was distilled over sodium and benzophenone. The other commercial reagents were not further purified.  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) experiments were performed on a JNM-LA300 FT-NMR instrument.

#### *Synthesis of dialkyl-substituted terminal olefin*

In a Shlenck tube 1-hexene (3.40 g, 5 mL, 40.5 mmol) was added to the mixture of  $\text{Cp}_2\text{ZrCl}_2$  (0.0876 g, 0.3 mmol), toluene (10 mL), and MAO (0.8 mL, 10 % toluene solution, 1.2 mmol (based on Al), molar ratio Al/Zr = 4). Then the reaction mixture was warmed to 50 °C and stirred for 24 hours. The reaction mixture was then quenched with 3 mol/L HCl and extracted with diethyl ether (2x30 mL). The extract was washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$ , filtrated and evaporated, leaving a colorless liquid substance. Column chromatography on silica gel with petroleum ether as eluent afforded the desired compound **2a**, isolated yield: 2.62 g (77%). The product was characterized by NMR, the spectrum of  $^1\text{H}$  NMR showed a characteristic single peak at 4.7 ppm, and the  $^{13}\text{C}$  NMR spectra showed two vinylidene carbon peaks at 108.3 (=CH<sub>2</sub>) and 150.5 (=C). Reactions of other  $\alpha$ -olefins were prepared according to the same procedure. The results were shown in **Table 1**.

**2-Butyl-1-octene (2a)**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 0.9 (m, 6H; CH<sub>3</sub>), 1.3-1.4 (m, 12H; CH<sub>2</sub>), 2.0-2.2 (m, 4H; CH<sub>2</sub>), 4.7 (s, 2H; =CH<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 14.1 (2CH<sub>3</sub>), 22.5 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 27.8 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 35.8 (CH<sub>2</sub>), 36.1 (CH<sub>2</sub>), 108.3 (=CH<sub>2</sub>), 150.5 (=C).

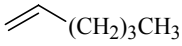
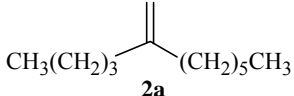
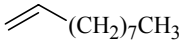
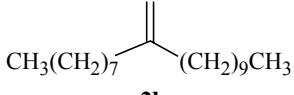
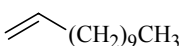
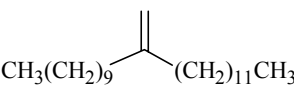
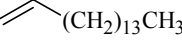
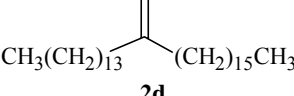
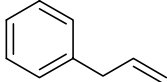
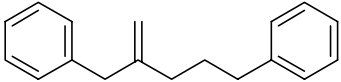
**2-Octyl-1-dodecene (2b)**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 0.90 (m, 6H; CH<sub>3</sub>), 1.3-1.4 (m, 28H; CH<sub>2</sub>), 2.0 (m, 4H; CH<sub>2</sub>), 4.7 (s, 2H; =CH<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 14.2 (2CH<sub>3</sub>), 22.7 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 27.8 (2CH<sub>2</sub>), 29.3-29.7 (8CH<sub>2</sub>), 31.9 (2CH<sub>2</sub>), 36.1 (2CH<sub>2</sub>), 108.3 (=CH<sub>2</sub>), 150.5 (=C).

**2-Decyl-1-tetradecene (2c)**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 0.90 (m, 6H; CH<sub>3</sub>), 1.3-1.4 (m, 38H; CH<sub>2</sub>), 2.0 (m, 4H; CH<sub>2</sub>), 4.7 (s, 2H; =CH<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 14.1 (2CH<sub>3</sub>), 22.7-36.1 (20CH<sub>2</sub>), 108.3 (=CH<sub>2</sub>), 150.5 (=C).

**2-Tetradecyl-1-octadecene (2d)**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 0.90 (m, 6H; CH<sub>3</sub>), 1.3-1.4 (m, 54H; CH<sub>2</sub>), 2.0 (m, 4H; CH<sub>2</sub>), 4.7 (s, 2H; =CH<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 14.2 (2CH<sub>3</sub>), 22.7-36.1 (28CH<sub>2</sub>), 108.3 (=CH<sub>2</sub>), 150.5 (=C).

**2-Methylene-1,5-diphenylpentane (2e)**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 1.7-1.8 (m, 2H; CH<sub>2</sub>), 2.00 (t, 2H; CH<sub>2</sub>), 2.60 (t, 2H; CH<sub>2</sub>), 3.3 (s, 2H; CH<sub>2</sub>), 4.8 (s, 1H; =CH), 4.8 (s, 1H; =CH), 7.1-7.3 (m, 10H; C<sub>6</sub>H<sub>5</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 29.4 (CH<sub>2</sub>), 35.0 (CH<sub>2</sub>), 35.5 (CH<sub>2</sub>), 43.0 (CH<sub>2</sub>), 111.3 (=CH<sub>2</sub>), 125.7 (CH), 126.0 (CH), 128.3 (4CH), 128.4 (2CH), 129.0 (2CH), 139.7 (C), 142.5 (C), 148.7 (=C).

**Table 1** The isolated yield of dialkyl-substituted terminal olefins and TON of catalyst <sup>a</sup>

Olefin	Product	Yield %	TON
 <b>1a</b>	 <b>2a</b>	77	52
 <b>1b</b>	 <b>2b</b>	92	41
 <b>1c</b>	 <b>2c</b>	72	12
 <b>1d</b>	 <b>2d</b>	75	32
 <b>1e</b>	 <b>2e</b>	79	20

a: 50 °C, 24 h, Al/Zr = 4.

## Discussion and Conclusion

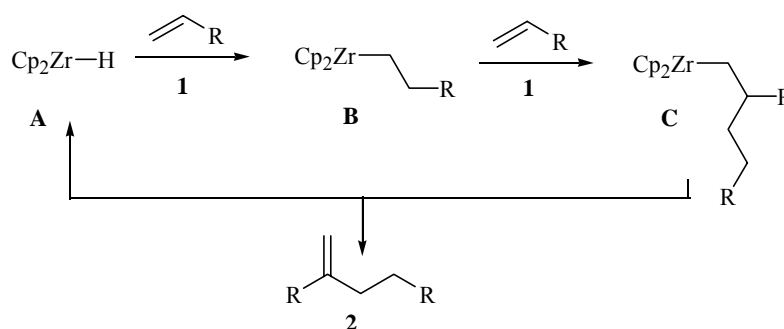
Zirconocene–MAO catalyst is currently introduced in industry as a new generation of Ziegler–Natta catalysts for the polymerization of olefins at high Al/Zr ratio<sup>8-12</sup>, but the use of low Al/Zr ratio has been much less frequently discussed. At the Al/Zr ratio of 1:1 this catalyst system can initiate the dimerization of olefins and intramolecular coupling of diene (cyclization)<sup>13</sup>. In our reaction, we found that the amount of expensive zirconocene dichloride could be decreased to Al/Zr ratio of 4:1 or 8:1. In this case, the zirconocene–MAO catalyst system exhibited high selectivity for the coupling reaction of two molecules of  $\alpha$ -olefins such as 1-hexene, 1-decene, 1-dodecene, 1-hexadecene and allylbenzene, which formed the dialkyl-substituted terminal olefins **2a-e**. No other oligomer was detected. The compounds **2b-d** were firstly synthesized by this method, and the yields were satisfactory (**Table 1**). The coupling reactions of three or more molecules of olefin took place, when the ratio of Al/Zr increased. It means that increase of molar ratio of Al/Zr could induce wider the distribution of products and less selectivity for the dimerization products.

The data shown in **Table 1** indicated that the coupling reaction was a catalytic reaction, the TON (turn over number) is from 12 to 52. The mechanism of the formation of the dialkyl-substituted terminal olefin can be proposed the catalytic action of zirconium-hydrido species **A** (**Scheme 2**)<sup>14-15</sup>, which formed *in situ* by the addition of the Zr-CH<sub>3</sub> complex to a 1-alkene, followed by  $\beta$ -H elimination of 2-methyl-1-alkene from the resulting Zr-alkyl complex. Insertion of the 1-alkene into the Zr-H bond are

the Zr-alkyl complex **B**, which can either  $\beta$ -H eliminate to re-form the starting materials or to insert into another equivalent of **1** to form **C**.  $\beta$ -Elimination of **C** formed **2** and regenerated the hydrid complex **A**.

We did not obtain the product of coupling reaction with this catalyst for monomer of propylene, but the solid polymer was obtained. It indicated that the relative rate of chain transfer to chain termination of propylene was higher than that of 1-hexene and other long chain  $\alpha$ -olefins, propylene molecules inserted into **C** and formed the high polymer.

**Scheme 2** Mechanism and catalytic cycle for the coupling reaction of  $\alpha$ -olefin



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### References

1. M. T. James, S. Mitra, *Angew. Chem. Int. Ed.*, **1999**, 38, 159.
2. E. De Vos Dirk, F. Sels Bert, R. Mattias, *et al.*, *Tetrahedron Lett.*, **1998**, 39, 3221.
3. D. J. O'Leary, H. E. Blackwell, R. A. Washenfelder, *et al.*, *Tetrahedron Lett.*, **1999**, 40, 1091.
4. J. A. Curiale, E. B. Frolov, *Org. Geochem.*, **1998**, 29 (1), 397.
5. Y. Tokunaga, T. Sakakura, M. Tanaka, *J. Mol. Catal.*, **1989**, 56, 305.
6. K. Avasthi, T. Baba, A. Suzuki, *Tetra. Lett.*, **1980**, 21, 945.
7. Y. Satoh, H. Serizawa, N. Miyaura, *et al.*, *Tetrahedron Lett.*, **1988**, 29 (15), 1811.
8. M. R. Ribeiro, A. Deffieux, M. F. Portela, *Ind. Eng. Chem. Res.*, **1997**, 36, 1224.
9. W. Spaleck, M. Anterg, J. Rohrmann, *et al.*, *Angew. Chem. Int. Ed. Engl.*, **1992**, 31 (10), 1347.
10. W. Kaminsky, A. Bark, R. Steiger, *J. Mol. Catal.*, **1992**, 74, 109.
11. K. Soga, H. J. Kim, T. Shiono, *Macromol. Chem. Phys.*, **1994**, 195, 3347.
12. N. M. Herzog, J. C. W. Chien, M. D. Ransch, *J. Organomet. Chem.*, **2002**, 654, 29.
13. J. Christoffers, R. G. Bergman, *Inorg. Chim. Acta*, **1998**, 270, 20.
14. A. R. Siedle, W. M. Lamanna, R. A. Newmark, J. N. Schroepfer, *J. Mol. Catal. A: Chem.*, **1998**, 128, 257.
15. M. C. Haag, C. Krug, J. Dupont, *et al.*, *J. Mol. Catal. A: Chem.*, **2001**, 169, 275.

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