Chinese Chemical Letters Vol. 11, No. 7, pp. 641–644, 2000

A Sterically Hindered Zirconocene Complex $(1,2\text{-}Ph_2C_5H_3)_2ZrCl_2$: Synthesis, Structure and Properties as Olefin Polymerization Catalyst

Fan ZHANG[1], Ying MU*[1], Yue Tao ZHANG[1], Cong Xi CHEN[1],
Hui Min ZHAI[1], Han HONG[2]

[1] Department of Chemistry, Jilin University, Changchun 130023
[2] Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract: An unbridged zirconocene complex bis(1,2-diphenylcyclopentadienyl)zirconium dichloride $[(1,2\text{-}Ph_2\text{-}C_5H_3)_2ZrCl_2]$ **1** has been synthesized and structurally characterized. When activated by MAO, **1** produces ultra-high molecular weight polyethylene with high melting transition temperature, as well as atactic oligopropylene with average molecular weight of ~1150 g mol^{-1}.

Keywords: Zirconium complex, metallocene catalyst, olefin polymerization.

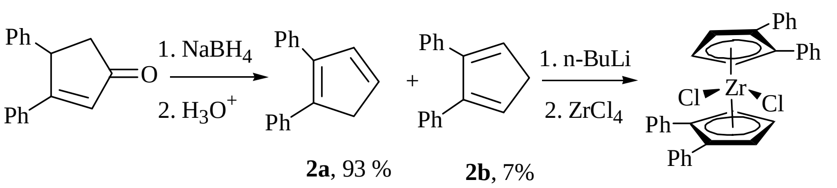
Since Kaminsky *et al.* discovered the highly active zirconocene dichloride/ methylaluminoxane (MAO) catalytic system for olefin polymerization[1], intensive research work has been focused on developing new group 4 metallocene catalysts for improving catalyst activities and polymer properties[2,3]. In the development of new metallocene catalyst systems, ligand design and modification have played an important role. It has been known that even minor modification of a given ligand framework could result in significant changes in catalyst activities and polymer properties[2]. In this respect, we have recently initiated a research program to investigate the effect of aryl-substituents at Cp rings on the catalytic properties of a number of unbridged zirconocene complexes. Herein we report the synthesis and crystal structure of a sterically hindered unbridged zirconocene dichloride $(1,2\text{-}Ph_2C_5H_3)_2ZrCl_2$ **1**, as well as its interesting properties as ethylene polymerization and propylene oligomerization catalyst.

Experimental

Complex **1** and its ligand 1,2-diphenylcyclopentadiene **2** were prepared from 3,4-diphenyl-2-cyclopentenone [4] as outlined in **Scheme 1**. **2** was synthesized according to the literature procedure[5]. Complex **1** was prepared as follows: To a solution of **2** (0.616 g, 2.82 mmol) in 30 mL of toluene was added 2.1 mL of BuLi (1.4 mol/L in hexane, 2.94 mmol) at –78 °C. The mixture was allowed to warm to room temp. and stirred overnight. $ZrCl_4$ (0.326 g, 1.40 mmol) was added at –78 °C and the reaction mixture was stirred for 8 h at room temp., then 18 h at 70 °C. The precipitate was filtered off and the solvent was removed to leave a pale yellow solid. Recrystallization from CH_2Cl_2/hexane gave pure **1**

(0.651 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.02 (t, J_{HH} 3.2, 1H, C_5H_3), 6.54 (d, J_{HH} 3.2Hz, 2H, C_5H_3), 7.24-7.34 (m, 20H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100MHz): δ 110.17, 117.94, 127.77 (C_5H_4), 128.12, 129.41, 129.96, 133.30 (C_6H_5); Calc. for [$C_{34}H_{26}Cl_2Zr$]: C, 68.46; H, 4.39; Found: C, 68.51; H, 4.33.

Scheme 1



2a, 93 %

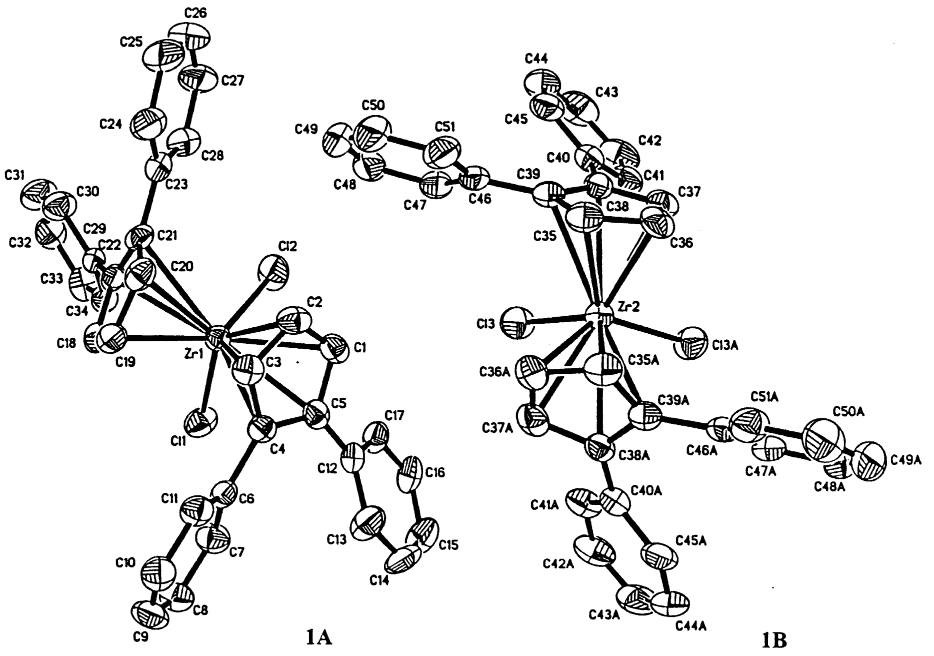
2b, 7%

1

Results and Discussion

^{1}H and ^{13}C NMR spectra of **1** reveal its time-averaged C_{2v} symmetry in solution due to rapid rotation of the cyclopentadienyl rings about the Cp(centroid)-Zr axis. The X-ray crystal structure[6] of **1** indicates that the compound exists in solid state as two torsional isomers in the unit cell, which are labeled with **A** and **B** respectively in **Figure 1**. The geometry about zirconium in **1** can be described as distorted tetrahedral. Two torsional isomers are in racemic-like conformation with near C_2 symmetry, in which one of the two phenyl groups at each Cp ring is above one of the two Cl atoms while the other one is in the direction away from the corresponding phenyl group at another Cp ring.

Figure 1. Molecule structure of complex **1**, showing the atom-labeling scheme.



The Cl-Zr-Cl angle is 94.25° for **1A** and 94.14° for **1B**, which are similar to the angles of *ca* 94° in analogous complexes[7]. The Cn-Zr-Cn (Cn is the centroid of Cp ring) angles (126.6° for **1A** and 126.9° for **1B**) are closed to the value of 126° found in $Zr(C_5H_4CH_2Ph)_2Cl_2$[8], but smaller than the one of 129.7° for $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}ZrCl_2$[9]. The angles (φ) between two Cp planes (61.6° for **1A** and 62.3° for **1B**) are much larger than the typical 51.4° observed for $(Bu^tCp)_2ZrCl_2$ and related compounds, even larger than that (60.5°) found in the staggered $[C_5H_4C(o\text{-}MePh){=}CH_2]_2ZrCl_2$[10] owing to the steric hindrance of the phenyl groups. The angles between the phenyl and Cp planes (31.2, 39.6, 32.9 and 50.1°) for isomer **1A** are quite different from those for isomers **1B** (32.3 and 37.8°), which are all larger than those (13.6 and 18.8°) observed for $(1,2\text{-}Me_2\text{-}4\text{-}PhC_5H_2)_2ZrCl_2$[11]. The Zr-Cl bond lengths (2.430(2) to 2.435(2) Å) are in the typical range for zirconocene dichlorides[10]. The distances of Zr-Cn (2.234, 2.237 Å for **1A** and 2.248 Å for **1B**) are somewhat longer than those (2.215 to 2.223 Å) observed in similar bulky zirconocene compounds[7,12].

Table 1. Ethylene polymerization results obtained with $(Ph_2Cp)_2ZrCl_2$ and Cp_2ZrCl_2 activated by MAO[a]

Catalyst	Al/Zr	Activity[b] × 10^{-3}	M_η[c] × 10^{-6}	T_m[d] (°C)
1	500	1.64	1.21	141.6
	1000	1.93	1.34	144.8
	1500	1.96	1.09	141.0
Cp_2ZrCl_2	500	1.19	0.46	132.2
	1000	2.26	0.43	131.9
	1500	3.69	0.42	131.5

[a] Polymerization conditions: solvent 50 ml of toluene, catalyst 1.7 μmol, time 1 hr, temp. 18 °C, ethylene pressure 6 bar. [b] kg PE (mol Zr)$^{-1}$ h^{-1}. [c] Measured in decahydronaphthalene at 135 °C.
[d] Determined with DSC at a heating rate of 10 °C min^{-1}.

Complex **1** was tested as polymerization catalyst for ethylene and propylene. Preliminary studies indicate that **1** has several features as catalyst: (1) Upon activation with MAO, **1** polymerizes ethylene with moderate catalytic activity at relatively low Al/Zr ratio compared to Cp_2ZrCl_2 (**Table 1**). Unlike Cp_2ZrCl_2, the catalytic activity of **1** does not decrease very much when Al/Zr ratio changes from 1500 to 500; (2) **1** produces ultra-high molecular weight polyethylene with high melting transition temperature. To our knowledge, the melting transition temperature of 144.8° is in the highest range observed so far for metallocene-polyethylene; (3) **1** shows relatively high activity for propylene oligomerization and produces oily oligopropylene[13]. ^1H and ^{13}C NMR analyses indicate that the obtained oligopropylene is atactic and ended with vinylidene group. No signal for internal olefinic groups and 2,1-units was observed, which indicates that β–H elimination is the only chain termination pathway and no 2,1-insertion takes place during the reaction. It is obvious that these observed features are resulted from the steric hindrance of the phenyl groups in the front side of the Cp rings of **1,** which efficiently prevents the catalyst from deactivation by bimolecular interaction and lowers the rate of chain termination by β-H elimination. Therefore, less MAO is required to keep the catalyst in active state and relative long polyethylene chain can be formed. For propylene polymerization, the four phenyl groups decrease the propylene coordination and insertion rate more severely than the chain termination rate, therefore lower the ratio of chain propagation rate to chain termination rate, which leads to the formation of oligopropylene.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 29734143 and No. 29672013) and the Sinopec.

References and notes

1. H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.*, **1980**, *181*, 99.
2. H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, **1995**, *34*, 1143, and references therein.
3. M. J. Bochmann, *J. Chem. Soc., Dalton Trans.*, **1996**, 225.
4. T. A. Geissmann, C. F. Koelsch, *J. Org. Chem.*, **1939**, *3*, 489.
5. R. Guy, C. Mahmoud, *C. R. Acad. Sci., Paris, Ser. C*, **1969**, *268*, 1960.
6. Crystallographic parameters have been deposited in the editorial office of CCL.
7. B. J. Grimmond, J. Y. Corey, N. P. Rath, *Organometallics* , **1999**, *18*, 404.
8. Y. Dusausoy, J. Protas, P. Renaut, B. Gautheron, G. Tainturier, *J. Organomet. Chem.*, **1978**, *157*, 167.
9. P. J. Chirik, M. W. Day, J. E. Bercaw, *Organometallics*, **1999**, *18*, 1873.
10. G. Erker, S. Wilker, C. Krüger, M. Nolte, *Organometallics*, **1993**, *12*, 2140.
11. K. Kimura, K. Takaishi, T. Matsukawa, T. Yoshimura, H. Yamazaki, *Chem. Lett.*, **1998**, 571.
12. G. Erker, R. Nolte, R. Aul, S. Wilker, C. Krüger, R. Noe, *J. Am. Chem. Soc.*, **1991**, *113*, 7594.
13. A typical oligomerization experiment was carried out under following conditions: 1.7 μ mol of **1** in 50 ml of toluene, Al/Zr: 1500, temperature: 20 °C, pressure: 1 bar, time: 1 hr. 7.1 g of colorless oily product was obtained with a catalytic activity of 4.2×10^6 g (mol Zr)$^{-1}$h^{-1}. ^{1}H NMR end group analysis on the product gives an average molecular weight of 1150 g mol^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.80-0.85 (- CH_3), 0.86-1.40 (- CH_2-), 1.55-1.65 (-Me CH-), 1.685 (=CCH_3-), 4.645, 4.723 (=CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.42 (-$CH_2CH_2CH_3$ end group), 19.5-21.3 (9 peaks, -CH_3), 22.25 (=C(CH_3)-), 27.3-33.1 (-MeCH-), 40.0-41.0 (-$CH_2CH_2CH_3$ end group), 44.0-48.0 (-CH_2-), 111.27 (CH_2=CMe-), 144.43 (CH_2=CMe-).

Received 6 December 1999
Revised 24 April 2000