



# Alkyne-functionalized metallocene complexes: Synthesis, structure, and catalytic ethylene polymerization

Min-Xiong Li<sup>a</sup>, Shan-Sheng Xu<sup>a</sup>, Hai-Bin Song<sup>a</sup>, Bin-Yuan Liu<sup>b</sup>, Bai-Quan Wang<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Elemento–Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

<sup>b</sup> Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, People's Republic of China

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## ABSTRACT

Reactions of phenylethynyl lithium with substituted cyclopentenones gave the corresponding pendant phenylethynyl substituted cyclopentadienes. Subsequent deprotonation and transmetalation with  $\text{TiCl}_4 \cdot 2\text{THF}$ ,  $\text{ZrCl}_4$ , and  $\text{Cp}^*\text{ZrCl}_3$  yielded the alkyne-functionalized metallocene complexes  $[\text{C}_5\text{Me}_4(\text{C}\equiv\text{CPh})_2\text{MCl}_2$  [ $\text{M} = \text{Ti}$  (**1**),  $\text{Zr}$  (**2**)],  $\text{Cp}^*[\text{C}_5\text{Me}_4(\text{C}\equiv\text{CPh})]\text{ZrCl}_2$  (**3**), and  $\text{Cp}^*[\text{C}_5\text{H}_2\text{R}'_2(\text{C}\equiv\text{CPh})]\text{ZrCl}_2$  [ $\text{R}' = \text{Me}$  (**4**),  $\text{Ph}$  (**5**)]. These complexes were fully characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS spectra, and elemental analysis. The molecular structure of **2** was determined by single crystal X-ray diffraction analysis. Ethylene polymerization was studied with these complexes in the presence of methylaluminoxane (MAO).

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## 1. Introduction

Since the discovery of methylaluminoxane (MAO) as an active cocatalyst in 1980 by Kaminsky and co-workers [1], metallocene olefin polymerization catalysts have been one of the most investigated research topics over the last few decades [2–4]. As a great advantage over the traditional heterogeneous Ziegler–Natta catalysts, a metallocene–MAO catalytic system has superbly high catalytic activity and can be tuned to tailor the polymer properties, such as molecular weight, molecular weight distribution, and stereochemistry, because the active species in these catalyst systems is the single-site active center. The steric and electronic effects of cyclopentadienyl ring substituents greatly influence the catalytic properties [5–7]. Thus it is possible to control their efficient catalytic properties by changing the ligand structure.

The cyclopentadienyl ligands with one or more alkyne groups as the ring substituents or the side chain functional groups have been extensively used to synthesize the alkyne-functionalized cyclopentadienyl transition metal complexes [8–27]. The alkyne group in these complexes not only acts as a donor of  $2\pi$  electrons to coordinate with the Lewis acidic metal center [8,9], but also as a reactive group to participate in the reactions [10–21]. However, up to now, alkyne-functionalized cyclopentadienyl transition-metal complexes have been mainly restricted to ferrocene and ruthenocene derivatives. Group 4 metal complexes with an alkyne-functionalized cyclopentadienyl ligand are very limited [22–27]. Recently, we reported the synthesis of alkynyl-substituted zirconocenes:  $\{\eta^5-$

$1,2\text{-R}_2\text{-4-(PhC}\equiv\text{C)C}_5\text{H}_2\text{)}_2\text{ZrCl}_2$  [ $\text{R} = \text{Me}$  (**6**),  $\text{Ph}$  (**7**)] [28] (Chart 1). They reacted with  $\text{Ru}_3(\text{CO})_{12}$  to form the unexpected Zr-decoordinated products. In this work, we will focus our research interest on the synthesis and catalysis of Group 4 metallocene complexes containing alkyne-functionalized cyclopentadienyl ligands.

## 2. Experimental

### 2.1. General considerations

All experimental manipulations were carried out under the atmosphere of dry argon using standard Schlenk technique. All solvents were distilled from appropriate drying agents under argon prior to use. Methylaluminoxane (MAO, 10% solution in toluene) was purchased from Arbemarle Co. Polymerization grade ethylene (Daqing Petrochemical Co., China) was used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV400 spectrometer and EI mass spectra on a VG ZAB-HS instrument. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Gel permeation chromatography (GPC) measurements were carried out via Waters Alliance GPC 2000 in 1,2,4-trichlorobenzene.  $\text{TiCl}_4 \cdot 2\text{THF}$  [29],  $\text{Cp}^*\text{ZrCl}_3$  [30], 1,2-Me<sub>2</sub>-4-(PhC≡C)C<sub>5</sub>H<sub>3</sub> (Cp<sup>II</sup>H), 1,2-Ph<sub>2</sub>-4-(PhC≡C)C<sub>5</sub>H<sub>3</sub> (Cp<sup>III</sup>H), **6**, and **7** [28] were synthesized according to literature procedures.

### 2.2. Synthesis of 1,2,3,5-Me<sub>4</sub>-4-(PhC≡C)C<sub>5</sub>H (Cp<sup>I</sup>H)

The ligand precursor Cp<sup>I</sup>H was prepared according to the procedure described for the synthesis of 2-phenylethynylindene [23]. To a solution of phenylacetylene (8.594 g, 84.15 mmol) dissolved in

\* Corresponding author. Tel./fax: +86 22 23504781.

E-mail address: [bqwang@nankai.edu.cn](mailto:bqwang@nankai.edu.cn) (B.-Q. Wang).

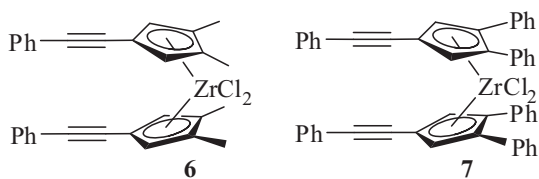


Chart 1.

THF (80 mL) was gradually added  $^n\text{BuLi}$  (84.15 mmol, 1.67 M in hexane) at 0 °C. After it was slowly warmed to room temperature and stirred for 5 h, a solution of 2,3,4,5-tetramethylcyclopent-2-enone (11.630 g, 84.15 mmol) in THF (30 mL) was added dropwise. The reaction mixture was stirred overnight and then quenched with saturated  $\text{NH}_4\text{Cl}$  aqueous solution (30 mL). The aqueous layer was extracted with diethyl ether, and the combined organics were dried over  $\text{Na}_2\text{SO}_4$ . After removal of solvents the residue was dissolved in diethyl ether (100 mL),  $\text{H}_2\text{SO}_4$  (3 M, 70 mL) was added, and then this mixture was stirred overnight. The reaction mixture was again quenched with a saturated  $\text{NH}_4\text{Cl}$  aqueous solution, separated, extracted with diethyl ether, and dried. After removal of solvents the residue was chromatographed over a silica gel column with hexane as eluent to give 8.044 g (43%) of  $\text{Cp}^{\text{I}}\text{H}$  as yellow oil. *Anal. Calc.* for  $\text{C}_{17}\text{H}_{18}$ : C, 91.84; H, 8.16. Found: C, 91.64; H, 8.36%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35 (br d,  $J = 5.1$  Hz, 2H, Ph-H), 7.18 (t,  $J = 7.5$ , 6.6 Hz, 3H, Ph-H), 2.77 (br d,  $J = 3.7$  Hz, 1H,  $\text{C}_5\text{H}$ ), 1.96 (s, 3H,  $\text{C}_5\text{-Me}$ ), 1.77 (s, 3H,  $\text{C}_5\text{-Me}$ ), 1.69 (s, 3H,  $\text{C}_5\text{-Me}$ ), 1.10 (d,  $J = 5.5$  Hz, 3H,  $\text{C}_5\text{-Me}$ ) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.3, 149.2, 143.4, 134.5, 131.0, 128.2, 127.2, 102.0, 95.4, 86.7, 51.5, 14.4, 13.4, 12.1, 10.8 ppm. MS (EI):  $m/z$  222.2 (100,  $\text{M}^+$ ).

### 2.3. Preparation of $\text{Cp}^{\text{I}}_2\text{TiCl}_2$ (**1**)

To a solution of  $\text{Cp}^{\text{I}}\text{H}$  (4.479 g, 20.15 mmol) in hexane (120 mL) was gradually added  $^n\text{BuLi}$  (20.04 mmol, 2.33 M in hexane) at 0 °C. Then it was slowly warmed to room temperature and stirred overnight. The resulting suspension was filtered and evaporated to dryness. THF (100 mL) and  $\text{TiCl}_4 \cdot 2\text{THF}$  (3.346 g, 10.02 mmol) was added to the reaction mixture through a cannula at  $-78$  °C and the reaction mixture was stirred at room temperature overnight. After removal of solvent under reduced pressure the residue was extracted with  $\text{CH}_2\text{Cl}_2$  and the solution was filtered through Celite. The solvent was removed in vacuo, and the crude product was recrystallized from a mixture of diethyl ether and hexane. About 2.756 g (49%) of **1** was obtained as red crystals. M.p.: 179–180 °C. *Anal. Calc.* for  $\text{C}_{34}\text{H}_{34}\text{Cl}_2\text{Ti}$ : C, 72.74; H, 6.10. Found: C, 72.51; H, 5.99%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55 (m, 2H, Ph-H), 7.34 (m, 3H, Ph-H), 2.47 (s, 6H,  $\text{C}_5\text{-Me}$ ), 2.28 (s, 6H,  $\text{C}_5\text{-Me}$ ) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 135.0, 134.2, 131.9, 128.7, 128.3, 122.7, 118.3, 98.9, 82.2, 14.4, 13.4 ppm. MS (EI):  $m/z$  221.1 (100,  $\text{Cp}^{\text{I}}$ ), 339.0 (20,  $\text{M}^+ - \text{Cp}^{\text{I}}$ ).

### 2.4. Preparation of $\text{Cp}^{\text{I}}_2\text{ZrCl}_2$ (**2**)

To a solution of  $\text{Cp}^{\text{I}}\text{H}$  (4.572 g, 20.56 mmol) in hexane (120 mL) was gradually added  $^n\text{BuLi}$  (20.50 mmol, 2.33 M in hexane) at 0 °C. Then it was slowly warmed to room temperature and stirred overnight. The resulting suspension was filtered and evaporated to dryness.  $\text{ZrCl}_4$  (2.389 g, 10.25 mmol) was added to the lithium salt, the flask was cooled to  $-78$  °C, and  $\text{CH}_2\text{Cl}_2$  (150 mL) was slowly added. After stirring overnight, the solution was filtered through Celite. The solvent was removed in vacuo, and the crude product was recrystallized from a mixture of diethyl ether and hexane to give yellow-green crystals. Yield: 2.480 g (40%). M.p.: 144–145 °C. *Anal. Calc.* for  $\text{C}_{34}\text{H}_{34}\text{Cl}_2\text{Zr}$ : C, 67.52; H, 5.67. Found: C, 67.32; H, 5.31%.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.41–7.38 (m, 2H, Ph-H), 7.31–7.27 (m, 3H, Ph-H), 2.27 (s, 6H,  $\text{C}_5\text{-Me}$ ), 2.04 (s, 6H,  $\text{C}_5\text{-Me}$ ) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 131.3, 129.0, 128.3, 128.1, 126.5, 123.3, 105.5, 95.4, 82.6, 12.8, 12.5 ppm. MS (EI):  $m/z$  601.9 (17,  $\text{M}^+$ ), 221.1 (10,  $\text{Cp}^{\text{I}}$ ), 380.9 (40,  $\text{M}^+ - \text{Cp}^{\text{I}}$ ).

### 2.5. Preparation of $\text{Cp}^{\text{I}}\text{Cp}^*\text{ZrCl}_2$ (**3**)

To a solution of  $\text{Cp}^{\text{I}}\text{H}$  (2.526 g, 11.36 mmol) in hexane (70 mL) was gradually added  $^n\text{BuLi}$  (11.42 mmol, 2.33 M in hexane) at 0 °C. Then it was slowly warmed to room temperature and stirred overnight. The resulting suspension was filtered and evaporated to dryness.  $\text{Cp}^*\text{ZrCl}_3$  (3.781 g, 11.36 mmol) was added to the lithium salt, the flask was cooled to  $-78$  °C, and methylene chloride (120 mL) was slowly added. After stirring overnight, the solution was filtered through Celite. The solvent was removed in vacuo, and the crude product was recrystallized from a mixture of diethyl ether and hexane to give a pale yellow solid. Yield: 1.768 g (30%). M.p. 141–142 °C. *Anal. Calc.* for  $\text{C}_{27}\text{H}_{32}\text{Cl}_2\text{Zr}$ : C, 62.52; H, 6.22. Found: C, 62.32; H, 6.31%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.55–7.51 (m, 2H, Ph-H), 7.40–7.31 (m, 3H, Ph-H), 2.09 (s, 6H,  $\text{C}_5\text{-Me}$ ), 2.08 (s, 15H,  $\text{Cp}^*$ ), 2.03 (s, 6H,  $\text{C}_5\text{-Me}$ ) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 131.0, 130.1, 128.6, 128.3, 124.7, 123.3, 105.1, 95.8, 83.3, 12.7, 12.3, 11.8 ppm. MS (EI):  $m/z$  516.0 (30,  $\text{M}^+$ ), 381.0 (95,  $\text{M}^+ - \text{Cp}^*$ ), 295.0 (40,  $\text{M}^+ - \text{Cp}^{\text{I}}$ ), 221.2 (17,  $\text{Cp}^{\text{I}}$ ), 135.1 (5,  $\text{Cp}^{**}$ ).

### 2.6. Preparation of $\text{Cp}^{\text{II}}\text{Cp}^*\text{ZrCl}_2$ (**4**)

By using a similar procedure to that described above, reaction of  $\text{Cp}^{\text{II}}\text{H}$  with  $^n\text{BuLi}$  and  $\text{Cp}^*\text{ZrCl}_3$  afforded complex **4** in 38% yield as yellow solid. M.p. 195–196 °C. *Anal. Calc.* for  $\text{C}_{25}\text{H}_{28}\text{Cl}_2\text{Zr}$ : C, 61.20; H, 5.75. Found: C, 61.23; H, 5.89%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.49–7.46 (m, 2H, Ph-H), 7.37–7.33 (m, 3H, Ph-H), 6.25 (s, 2H,  $\text{C}_5\text{H}_2$ ), 2.08 (s, 15H,  $\text{Cp}^*$ ), 2.05 (s, 6H,  $\text{C}_5\text{-Me}$ ) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 131.2, 128.4, 127.6, 124.9, 123.0, 120.7, 100.6, 91.1, 83.3, 13.3, 12.3 ppm. MS (EI):  $m/z$  353.0 (72,  $\text{M}^+ - \text{Cp}^*$ ), 295.0 (86,  $\text{M}^+ - \text{Cp}^{\text{II}}$ ), 135.1 (7,  $\text{Cp}^{**}$ ).

### 2.7. Preparation of $\text{Cp}^{\text{III}}\text{Cp}^*\text{ZrCl}_2$ (**5**)

By using a similar procedure to that described above, reaction of  $\text{Cp}^{\text{III}}\text{H}$  with  $^n\text{BuLi}$  and  $\text{Cp}^*\text{ZrCl}_3$  afforded complex **5** in 32% yield as yellow solid. M.p. 277–278 °C. *Anal. Calc.* for  $\text{C}_{35}\text{H}_{32}\text{Cl}_2\text{Zr}$ : C, 68.38; H, 5.25. Found: C, 68.32; H, 5.31%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.52 (m, 2H, Ph-H), 7.38 (m, 7H, Ph-H and  $\text{C}_5\text{-Ph}$ ), 7.28 (m, 6H, Ph-H and  $\text{C}_5\text{-Ph}$ ), 6.72 (s, 2H,  $\text{C}_5\text{H}_2$ ), 1.89 (s, 15H,  $\text{Cp}^*$ ) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 132.7, 131.4, 130.0, 128.6, 128.5, 128.0, 127.7, 125.9, 122.8, 103.2, 92.4, 82.9, 12.1 ppm. MS (EI):  $m/z$  612.1 (11,  $\text{M}^+$ ), 476.9 (7,  $\text{M}^+ - \text{Cp}^*$ ), 295.0 (20,  $\text{M}^+ - \text{Cp}^{\text{III}}$ ).

### 2.8. Crystallographic studies

Single crystals of complex **2** suitable for X-ray diffraction were obtained from hexane/ $\text{Et}_2\text{O}$  solution at  $-20$  °C. Data collections were performed with a Rigaku Saturn 70 diffractometer equipped with a rotating anode system at 113(2) K by using graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\omega - 2\theta$  scans,  $\lambda = 0.71073$  Å). Semi-empirical absorption corrections were applied. The structure was solved by direct methods and refined by full-matrix least squares. All calculations were performed by using the SHELXL-97 program system. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. The crystal data and summary of X-ray data collection are presented in Table 1.

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