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

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ABSTRACT

Reactions of phenylethynyl lithium with substituted cyclopentenones gave the corresponding pendant phenylethynyl substituted cyclopentadienes. Subsequent deprotonation and transmetallation with $TiCl_4{\cdot}2THF$, $ZrCl_4$, and Cp^*ZrCl_3 yielded the alkyne-functionalized metallocene complexes $[C_5Me_4(C{\equiv}CPh)]_2MCl_2$ [M = Ti (**1**), Zr (**2**)], $Cp^*[C_5Me_4(C{\equiv}CPh)]ZrCl_2$ (**3**), and $Cp^*[C_5H_2R'_2(C{\equiv}CPh)]ZrCl_2$ [R′ = Me (**4**), Ph (**5**)]. These complexes were fully characterized by ^1H NMR, ^{13}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).

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 2π 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: $\{\eta^5\text{-}[1,2\text{-}R_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_2]\}_2ZrCl_2$ [R = Me (**6**), Ph (**7**)] [28] (Chart 1). They reacted with $Ru_3(CO)_{12}$ 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. ^1H and ^{13}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. $TiCl_4{\cdot}2THF$ [29], Cp^*ZrCl_3 [30], $1,2\text{-}Me_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_3$ ($Cp^{II}H$), $1,2\text{-}Ph_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_3$ ($Cp^{III}H$), **6**, and **7** [28] were synthesized according to literature procedures.

2.2. Synthesis of $1,2,3,5\text{-}Me_4\text{-}4\text{-}(PhC{\equiv}C)C_5H$ (Cp^IH)

The ligand precursor Cp^IH 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

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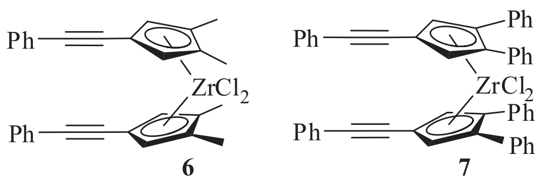


6 **7**

Chart 1.

THF (80 mL) was gradually added ^{n}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 NH_4Cl aqueous solution (30 mL). The aqueous layer was extracted with diethyl ether, and the combined organics were dried over Na_2SO_4. After removal of solvents the residue was dissolved in diethyl ether (100 mL), H_2SO_4 (3 M, 70 mL) was added, and then this mixture was stirred overnight. The reaction mixture was again quenched with a saturated NH_4Cl 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 Cp^{I}H as yellow oil. *Anal.* Calc. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.64; H, 8.36%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, C_5H), 1.96 (s, 3H, C_5-Me), 1.77 (s, 3H, C_5-Me), 1.69 (s, 3H, C_5-Me), 1.10 (d, *J* = 5.5 Hz, 3H, C_5-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 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, M$^+$).

2.3. Preparation of $Cp^I_2TiCl_2$ (**1**)

To a solution of Cp^{I}H (4.479 g, 20.15 mmol) in hexane (120 mL) was gradually added ^{n}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 $TiCl_4 \cdot 2THF$ (3.346 g, 10.02 mmol) were 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 CH_2Cl_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 $C_{34}H_{34}Cl_2Ti$: C, 72.74; H, 6.10. Found: C, 72.51; H, 5.99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 2H, Ph-H), 7.34 (m, 3H, Ph-H), 2.47 (s, 6H, C_5-Me), 2.28 (s, 6H, C_5-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 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, Cp^{I+}), 339.0 (20, M$^+$−Cp^I).

2.4. Preparation of $Cp^I_2ZrCl_2$ (**2**)

To a solution of Cp^{I}H (4.572 g, 20.56 mmol) in hexane (120 mL) was gradually added ^{n}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. $ZrCl_4$ (2.389 g, 10.25 mmol) was added to the lithium salt, the flask was cooled to −78 °C, and CH_2Cl_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 $C_{34}H_{34}Cl_2Zr$: C, 67.52; H, 5.67. Found: C, 67.32; H, 5.31%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.41–7.38 (m, 2H, Ph-H), 7.31–7.27 (m, 3H, Ph-H), 2.27 (s, 6H, C_5-Me), 2.04 (s, 6H, C_5-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 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, M$^+$), 221.1 (10, Cp^{I+}), 380.9 (40, M$^+$−Cp^I).

2.5. Preparation of $Cp^ICp^*ZrCl_2$ (**3**)

To a solution of Cp^{I}H (2.526 g, 11.36 mmol) in hexane (70 mL) was gradually added ^{n}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. Cp^*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 $C_{27}H_{32}Cl_2Zr$: C, 62.52; H, 6.22. Found: C, 62.32; H, 6.31%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.55–7.51 (m, 2H, Ph-H), 7.40–7.31 (m, 3H, Ph-H), 2.09 (s, 6H, C_5-Me), 2.08 (s, 15H, Cp*), 2.03 (s, 6H, C_5-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 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, M$^+$), 381.0 (95, M$^+$−Cp*), 295.0 (40, M$^+$−Cp^I), 221.2 (17, Cp^{I+}), 135.1 (5, Cp^{*+}).

2.6. Preparation of $Cp^{II}Cp^*ZrCl_2$ (**4**)

By using a similar procedure to that described above, reaction of Cp^{II}H with ^{n}BuLi and Cp^*ZrCl_3 afforded complex **4** in 38% yield as yellow solid. M.p. 195–196 °C. *Anal.* Calc. for $C_{25}H_{28}Cl_2Zr$: C, 61.20; H, 5.75. Found: C, 61.23; H, 5.89%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.49–7.46 (m, 2H, Ph-H), 7.37–7.33 (m, 3H, Ph-H), 6.25 (s, 2H, C_5H_2), 2.08 (s, 15H, Cp*), 2.05 (s, 6H, C_5-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 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, M$^+$−Cp*), 295.0 (86, M$^+$−Cp^{II}), 135.1 (7, Cp^{*+}).

2.7. Preparation of $Cp^{III}Cp^*ZrCl_2$ (**5**)

By using a similar procedure to that described above, reaction of Cp^{III}H with ^{n}BuLi and Cp^*ZrCl_3 afforded complex **5** in 32% yield as yellow solid. M.p. 277–278 °C. *Anal.* Calc. for $C_{35}H_{32}Cl_2Zr$: C, 68.38; H, 5.25. Found: C, 68.32; H, 5.31%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.52 (m, 2H, Ph-H), 7.38 (m, 7H, Ph-H and C_5-Ph), 7.28 (m, 6H, Ph-H and C_5-Ph), 6.72 (s, 2H, C_5H_2), 1.89 (s, 15H, Cp*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 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, M$^+$), 476.9 (7, M$^+$−Cp*), 295.0 (20, M$^+$−Cp^{III}).

2.8. Crystallographic studies

Single crystals of complex **2** suitable for X-ray diffraction were obtained from hexane/Et_2O 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 Mo Kα 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.

Table 1
Summary of crystallographic data for **2**.

Empirical formula	$C_{34}H_{34}Cl_2Zr$
Formula weight	604.73
Crystal system	orthorhombic
Space group	*Pcca*
a (Å)	16.705(3)
b (Å)	12.082(2)
c (Å)	17.047(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3440.5(12)
Z	4
D_{calc} (g cm^{-3})	1.167
μ (mm^{-1})	0.493
$F(0\,0\,0)$	1248
Crystal size (mm)	0.18 × 0.16 × 0.10
Maximum 2θ (°)	50.04
Number of reflections collected	24 214
Number of independent reflections (R_{int})	2948/0.0359
Number of parameters	172
Goodness-of-fit (GOF) on F^2	1.062
R_1, wR_2 [$I > 2\sigma(I)$]	0.0324, 0.0831
R_1, wR_2 (all data)	0.0351, 0.0856
Largest difference peak and hole (e Å^{-3})	0.356, −0.498

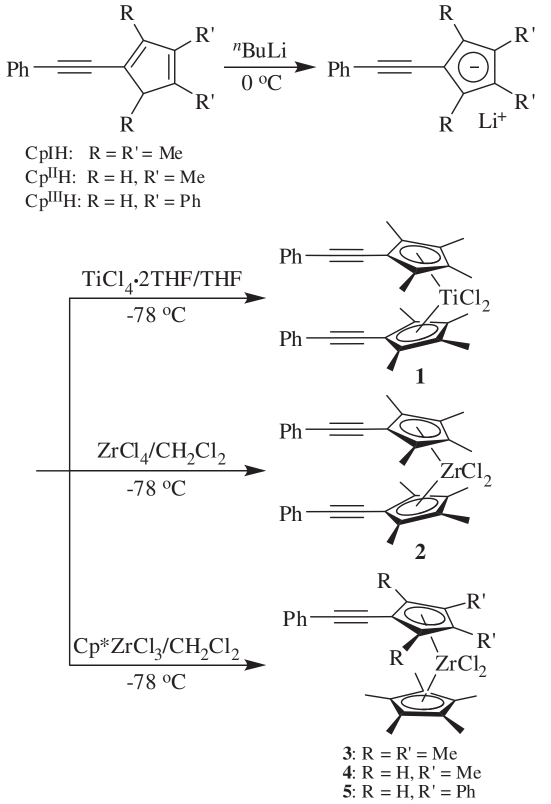
2.9. Ethylene polymerization

Ethylene polymerization experiments were carried out in a 100 mL Schlenk flask with magnetic stirring. A prescribed amount of MAO was added to 40 mL of toluene saturated with ethylene (1 atm) in the flask, and the reactor was placed in an oil bath at the desired temperature. Then the metallocene catalyst (5 μmol in 10 mL of toluene) was injected into the flask via syringe and the reaction was started. After 30 min, all the reactions were quenched by addition of an acidified ethanol solution (10% HCl in EtOH) and the resulting polyethylene was precipitated by the addition of 200 mL of ethanol. The precipitated polymer was washed with ethanol and water and dried at 60 °C in vacuo to a constant weight.

3. Results and discussion

3.1. Synthesis of complexes 1–5

The titanium and zirconium complexes **1** and **2** were prepared by reactions of the lithium salts of the corresponding ligands with $TiCl_4\cdot 2THF$ and $ZrCl_4$ in 49% and 40% yields, respectively (Scheme 1). The zirconium complexes **3**–**5** were prepared through the reaction of the lithium salts of the corresponding ligands with Cp^*ZrCl_3. Complexes **1**–**5** are stable to air and moisture in the solid state and could be exposed to air for several hours without obvious decomposition, but they decomposed readily in solution when exposed to air. Most of them are quite soluble in Et_2O, CH_2Cl_2, and THF, while **5** is hardly soluble in Et_2O. The ^1H NMR spectra show two singlets for the methyl protons at 2.47 and 2.28 ppm for **1**, and 2.27 and 2.04 ppm for **2**. This indicates that they consist of two equivalent cyclopentadienyl units and have C_{2v} symmetry in the solution. The ^1H NMR spectra of **3**–**5** all show a strong singlet for the Cp* protons at 2.08, 2.08, and 1.89 ppm, respectively. Two singlets at 2.09 and 2.03 ppm for the methyl protons in **3**, two singlets at 6.25 and 2.05 ppm for the cyclopentadienyl and methyl protons in **4**, and one singlet at 6.72 ppm for the cyclopentadienyl protons in **5** are also observed. The ^{13}C NMR spectra of **1**–**5** all show the signals of the two alkyne carbons at 98.9–91.1 and 83.3–82.2 ppm. The mass spectra of zirconium complexes **2**, **3**, and **5** all show the molecular ion peaks.



Scheme 1.

3.2. X-ray structure of 2

The molecular structure of **2** was determined by X-ray diffraction (Fig. 1). It has a C_2-symmetry axis through the zirconium atom. The phenylethynyl substituents are almost linear [C(1)–C(10)–C(11) 178.03(19), C(10)–C(11)–C(12) 178.15(18)°], which are similar to that of $[1,2\text{-}Ph_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_2]_2ZrCl_2$ [28] and the 2-phenylethynylindenyl zirconium complexes [26],[27]. The C(10)–C(11) bond length [1.374(3) Å] is significantly longer than those in $[1,2\text{-}Ph_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_2]_2ZrCl_2$ [1.184(3) and 1.193(3) Å] [28] and the values of substituted acetylenes. The two phenylethynyl substituents are oriented toward the different lateral sector of the bent-metallocene wedge. The cyclopentadienyl ring and the phenyl ring of the phenylethynyl fragment are not coplanar with a dihedral angle of 34.3°. The Zr–C(Cp) bond lengths are very different [2.5190–2.854 Å] due to the presence of the two phenylethynyl fragments. The Cl–Zr–Cl angle is 106.09(4)°, which is evidently larger than those in $[1,2\text{-}Ph_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_2]_2ZrCl_2$ [98.17(3)°] [28], $(PhC_5Me_4Cp)_2ZrCl_2$ [94.75(2)°] [31], and $(C_5Me_4H)_2ZrCl_2$ [97.61(9)°] [32]. The Cent–Zr–Cent angle (137.5°) is close to 136.34(2)° for $(PhC_5Me_4Cp)_2ZrCl_2$, but larger than the those found in $(C_5Me_4H)_2ZrCl_2$ [133.1(1)°] and $[1,2\text{-}Ph_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_2]_2ZrCl_2$ [130.30°]. The dihedral angle between the two cyclopentadienyl planes (47.9°) is close to the value of 46.0(1)° for $(PhC_5Me_4Cp)_2ZrCl_2$, but smaller than those for $(C_5Me_4H)_2ZrCl_2$ [53.7(4)°] and $[1,2\text{-}Ph_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_2]_2ZrCl_2$ [56°]. The Zr–Cent (2.318 Å) distance is longer than those in $[1,2\text{-}Ph_2\text{-}4\text{-}(PhC{\equiv}C)C_5H_2]_2ZrCl_2$ (2.248, 2.245 Å), $(PhC_5Me_4Cp)_2ZrCl_2$ [(2.258(1) Å], and $(C_5Me_4H)_2ZrCl_2$ [(2.226(3) Å].

3.3. Ethylene polymerization

When activated with MAO all the zirconium complexes are effective catalysts for ethylene polymerization. The catalytic

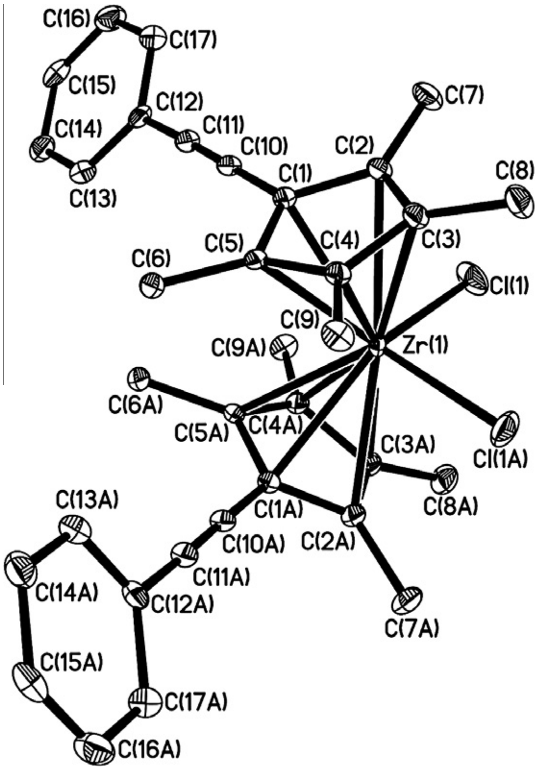


Fig. 1. ORTEP diagram of **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] are: Zr(1)–Cl(1) 2.6734(7), Zr(1)–C(1) 2.519(2), Zr(1)–C(2) 2.584(2), Zr(1)–C(3) 2.731(2), Zr(1)–C(4) 2.854(2), Zr(1)–C(5) 2.625(2), C(1)–C(10) 1.638(3), C(10)–C(11) 1.374(3), C(11)–C(12) 1.655(3), Cl(1)–Zr(1)–Cl(1A) 106.09(4), C(1)–C(10)–C(11) 178.0(2), C(10)–C(11)–C(12) 178.2(2).

Table 3
Ethylene polymerization catalyzed by complexes **1**–**7**/MAO[a].

Catalyst	T_p (°C)	Yield (g)	A [b] (10^6)	M_n [c]	M_w [c]	PDI
1	20	0.2761	0.11			
	40	0.4727	0.19			
	60	0.2279	0.09			
	80	0.2462	0.10			
2	20	1.2914	0.52	6765	20971	3.10
	40	2.1568	0.86			
	60	1.6593	0.66	2183	4053	1.86
	80	1.6036	0.64	56152	91269	1.62
3	20	0.1492	0.06			
	40	1.6045	0.64			
	50	1.1713	0.47			
	60					
4	20	0.8775	0.35	5764	41597	7.22
	40	1.9676	0.79	15769	30370	1.92
	60	2.9522	1.18	5601	8285	1.48
	80	2.4736	0.99	2789	5960	2.14
5	20	1.7112	0.68	56633	101834	1.80
	40	4.6795	1.87	2183	4059	1.86
	60	3.0982	1.24	1276	2460	1.93
	80	1.9776	0.79			
6	20	2.0010	0.80	45189	68014	1.50
	40	1.9871	0.79	20103	33783	1.68
	60	2.1235	0.85	12271	29628	2.41
	80	1.6237	0.65	13005	16983	1.30
7	20	1.7633	0.70			
	40	0.3767	0.15			
	60	1.2891	0.52			
	80	1.0595	0.42			
Cp_2ZrCl_2	20	1.5721	0.63			
	40	1.7285	0.69			
	60	3.1223	1.25			
	80	1.9007	0.76			

[a] Polymerization conditions: in 50 mL of toluene, cat. 5.0 μmol, [Al]/[Zr] = 2000, $P_{ethylene}$ = 0.1 MPa, t = 0.5 h.
[b] A = activity in units of (g of polymer) (mol of Zr)$^{-1}$ h^{-1}.
[c] M_n, M_w (g/mol), and PDI were determined by GPC.

activity of **6** increases with the increase of Al/Ti ratio from 1000 to 2000. But further increase of the Al/Ti ratio results in a decrease in the catalytic activity (Table 2). Using the Al/Ti ratio of 2000, all complexes were studied as precatalysts for ethylene polymerization (Table 3). For comparison, the polymerization experiment catalyzed by Cp_2ZrCl_2/MAO was also carried out. As expected, the zirconocenes **2**–**7** show higher activities than the titanocene **1**. The unsymmetrical phenylethynyl dimethyl or diphenyl cyclopentadienyl zirconocenes **4** and **5** show higher activities than the unsymmetrical phenylethynyl tetramethylcyclopentadienyl zirconocenes **2** and **3**, and the symmetrical phenylethynyl dimethyl or diphenyl cyclopentadienyl zirconocenes **6** and **7**, probably due to the steric effect. At 40 °C the phenylethynyl diphenylcyclopentadienyl zirconocene **5** shows the highest activity, 1.87×10^6 g (mol of Zr)$^{-1}$ h^{-1}, which is even higher than that of Cp_2ZrCl_2. Above 50 °C, complex **3** is inactive, which reflects the catalyst is unstable at high temperature. The polyethylenes produced by the zirconocene complexes show a narrow molecular weight distribution (M_w/M_n) except complex **4** at 20 °C, suggesting that the polymerization proceeded with single catalytic active species. At 20 °C, **4**/MAO system affords polyethylene with a bimodal molecular weight distribution, while polyethylene with a monomodal distribution is obtained at 40 °C or above. There is a similar report in the literature [33] and it was attributed to the highly exothermal nature of the polymerization reaction. The catalytic system produces highly active species for ethylene polymerization at 20 °C; however, the active species would probably be changed into multiply active sites because of reaction temperature fluctuations during the exothermal polymerization. The low molecular weight of polyethylene could be attributed to the presence of the two phenylethynyl fragments, which may promote β-H elimination.

Table 2
Ethylene polymerization catalyzed by complex **6**/MAO[a].

Catalyst	Al/Zr	Yield (g)	A [b] (10^6)
6	1000	0.8064	0.32
	1500	1.1700	0.47
	2000	1.9871	0.79
	2500	1.7560	0.70

[a] Polymerization conditions: in 50 mL of toluene, cat. 5.0 μmol, T_p = 40 °C, $P_{ethylene}$ = 0.1 MPa, t = 0.5 h.
[b] A = activity in units of (g of polymer) (mol of Zr)$^{-1}$ h^{-1}.

In conclusion, a series of alkyne-functionalized titanocene and zirconocene complexes **1**–**5** have been synthesized. When activated with MAO they are effective catalysts for ethylene polymerization. Among them the unsymmetrical phenylethynyl diphenylcyclopentadienyl pentamethylcyclopentadienyl zirconocene **5** shows the highest activity at 40 °C, which is even higher than that of Cp_2ZrCl_2. The active species is likely to be uniform, giving PEs with narrow molecular weight distribution and low molecular weight.

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Appendix A. Supplementary data

CCDC 801558 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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