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Synthesis of bis(1,2,3-substituted cyclopentadienyl)zirconium dichloride derivatives and their use in ethylene polymerization

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Abstract

Catalytic Pauson–Khand reaction products with norbornadiene could be effectively transformed to trisubstituted cyclopentadienes, which have been used to synthesize a series of unbridged bis(1-R′-2-R-3-R′-trisubstituted cyclopentadienyl)zirconium dichlorides **3** (R = R′ = Ph), **4**(R = Ph, R′ = Me), **21**(R = *n*-Bu, R′ = Me), **22**(R = *t*-Bu, R′ = Me), **23**(R = $(CH_2)_4OMe$), R′ = Me), and **24**(R = *n*-Bu, R′ = Ph). The crystal structure of **24** was determined by X-ray crystallography. These zirconium complexes in the presence of methylaluminoxane (MAO) show activities for the polymerization of ethylene. The activities are in the following order: **21** > **4** > **22** ~ **23** ~ Cp_2ZrCl_2 > **3** ~ **24**. The activity of **21** is four times higher than that of Cp_2ZrCl_2 under similar conditions.

Keywords: Ethylene; Polymerization; Pauson–Khand reaction; Zirconocene

1. Introduction

Cyclopentadienyl ligands are one of the most popular ligands in organometallic chemistry and the development of efficient approaches to the generation of highly substituted or functionalized cyclopentadienyl ligands is of continuing importance [1]. Substitution or functionalization of the cyclopentadienyl ring modifies the steric and electronic properties of the metal center and implies important changes in the structural and chemical behavior of this type of compound [2]. The chemical and physical properties of Group 4 bent metallocenes can be varied over a wide range by modification of the substituents on the cyclopentadienyl ring [3]. The Group 4 metallocene compounds have attracted much attention due to their use as catalyst precursors for the homogeneous polymerization of olefins [4]. Thus, many research groups are involved in the design of ligands to tailor the catalytic activity and product properties [5]. However, a limited range of metallocenes containing such ligands have been prepared and studied due to the absence of the generalized synthetic method of the substituted cyclopentadiene. Several years ago, we reported the general method of preparation of 1,2-disubstituted and 1,2,3-trisubstituted cyclopentadienyl ligands via the retro-Diels–Alder reaction of the intermolecular Pauson–Khand reaction products (Scheme 1) [6].

Herein we report the synthesis and characterization of a series of unbridged bis(1,2,3-trisubstituted cyclopentadienyl)zirconium dichlorides and their use in the polymerization of ethylene.

2. Experimental

2.1. General considerations

Reactions were carried out under an argon or a nitrogen atmosphere using standard Schlenk tech-

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Table 1
X-ray data collection and structure refinement for **24**

Formula	$C_{42}H_{42}Cl_2Zr$
Formula weight	708.88
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	19.576(2)
b (Å)	19.129(2)
c (Å)	21.020(5)
β (°)	97.505(9)
V (Å^3)	7804(2)
Z	8
D_{calc} (g cm^{-3})	1.207
μ (mm^{-1})	0.444
T_{max}	0.2975
T_{min}	0.2572
No. of reflections measured	10417
No. of reflections with $I>2\sigma(I)$	10033
No. of parameters used	731
2θ range (°)	3.5–45.0
GOF	1.055
Max., min. in $\Delta\rho$ (Å^{-3})	0.565, −0.479
R	0.0648
wR_2 [a]	0.1516

[a] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

niques. Methylaluminoxane (MAO) was purchased from Akzo (6.4 wt% of Al, MMAO type 4), and all other reagents were purchased from Aldrich and used without further purification. Diethyl ether and tetrahydrofuran (THF) were distilled from Na and benzoketone. Hexane and toluene were purified by distillation over Na/K alloys under argon. Ethylene was purchased from Matheson as high purity grade (99.9%) and dried by passing through the columns of activated molecular sieves and copper. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-300 spectrometer. Elemental analyses were carried out at Seoul National University on a Carlo Erba EA 1108 elemental analyzer. Gel permeation chromatograms (GPC) were obtained at 140°C in trichlorobenzene using Waters model 150-C + GPC and the data were analyzed using a polystyrene analyzing curve. Melting points were measured on a Thomas Hoover capillary melting point apparatus 6427-H 10 and not corrected. Compounds **1**, **2**, and **9** were described previously [6,7], but their characterization had not been reported in detail. Thus, their characterization is reported here. *t*-Butylacetylene has been prepared by the known method [8].

2.1.1. Compound **1**

White solid; m.p. 150–153°C; ^{1}H-NMR ($CDCl_3$): δ 7.4–7.1 (m, 15 H), 6.46 (s, 1 H), 3.55 (s, 2 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.40, 142.51, 141.96, 136.95, 136.67, 136.52, 129.91, 129.34, 128.19, 128.06, 128.01, 127.75, 126.78, 126.71, 126.32 ppm. HRMS (M^+) Calc. 294.1409, observed 294.1409.

2.1.2. Compound **2**

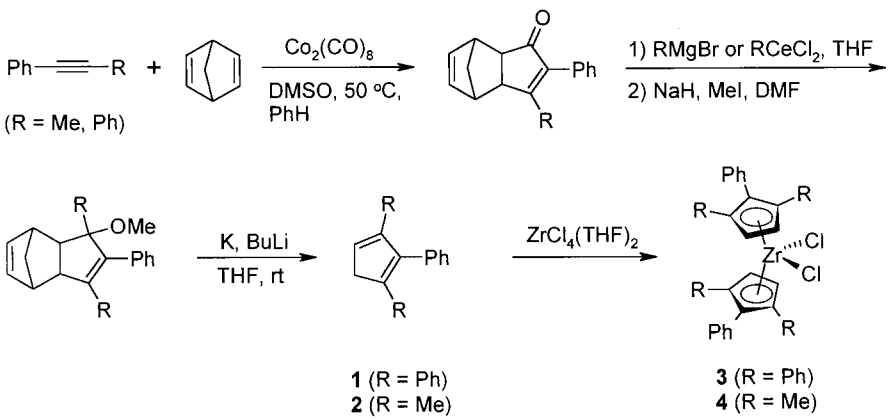
Oil. ^{1}H-NMR ($CDCl_3$): δ 7.39–7.19 (m, 5 H), 5.95 (m, 1 H), 2.96 (m, 2 H), 1.99 (s, 3 H), 1.88 (m, 3 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 143.72, 142.56, 140.43, 129.70, 128.45, 126.81, 124.73, 44.75, 15.64, 15.08 ppm. HRMS (M^+) Calc. 170.1096, observed 170.1098.

2.1.3. Compound **9**

Oil; ^{1}H-NMR ($CDCl_3$): δ 6.18 (m, 1 H), 6.13 (m, 1 H), 3.12 (s, 1 H), 2.74 (s, 1 H), 2.31 (d, 18 Hz, 1 H), 2.13 (m, 1 H), 1.83 (t, 8.0 Hz, 1 H), 1.59–1.20 (m, 8 H), 1.23 (d, 6.5 Hz, 3 H), 1.07 (d, 9.1 Hz, 1 H), 0.89 (t, 6.8 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 219.09, 138.67, 137.87, 61.12, 54.70, 49.12, 47.11, 45.32, 44.93, 40.41, 29.56, 27.48, 23.48, 21.52, 14.39 ppm. Anal. Found: C, 81.97; H, 10.47. $C_{15}H_{22}O$ Anal. Calc.: C, 82.52; H, 10.16%. HRMS (M^+) Calc. 218.1671, observed 218.1678.

2.2. General procedure for the Pauson–Khand reaction of alkyne with norbornadiene

$Co_2(CO)_8$ (1 mol%) was added to a solution of alkyne and norbornadiene in methylene dichloride. The



Scheme 1.

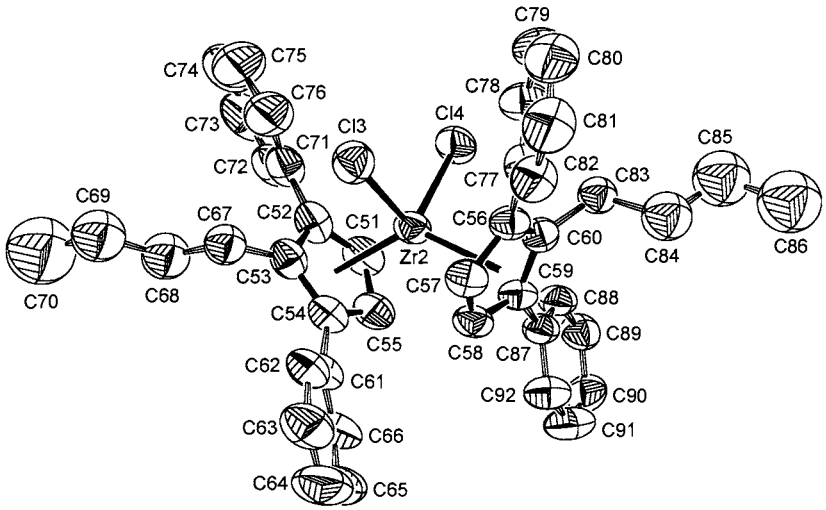


Fig. 1. ORTEP drawing of **24**, with atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angle (°): Zr2–Cl3, 2.427(2); Zr2–C51, 2.486(7); Zr2–C52, 2.570(7); C52–C53, 1.433(9); C53–C54, 1.424(10); C51–C55 1.392(9); C53–C67, 1.490(10); C52–C71, 1.486(11); Cl3–Zr2–Cl4, 99.06(7).

solution was subjected to an appropriate pressure of CO and heated at 120°C for 1 day. After the solution was cooled to room temperature (r.t.), it was filtered, concentrated, and chromatographed on a silica gel column. After the solvent was removed, the corresponding Pauson–Khand product was obtained.

2.3. Compound *3*

Compound **3** was prepared by using the same methodology as described for **21** (see Section 2.17). The reaction time was 7 days instead of 40 h. Products were extracted with hot toluene. Yield: 54%. Yellow solid. M.p. 300°C (dec.). ^{1}H-NMR ($CDCl_3$): δ 7.24–7.10 (m, 15 H), 6.41 (s, 2 H) ppm. Anal. Found: C, 73.70; H, 4.52. $C_{46}H_{34}Cl_2Zr$ Anal. Calc.: C, 73.78; H, 4.58%.

2.4. Compound *4*

Compound **4** was prepared by using the same methodology as described for **16** (see Section 2.12). Products were extracted with hot toluene and hexane solution (v/v, 3:1). Yield: 54%. Light yellow solid. M.p. 221–222°C. ^{1}H-NMR ($CDCl_3$): δ 7.40–7.25 (m, 5 H), 5.91 (s, 2 H), 2.16 (s, 6 H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ 133.53, 131.44, 130.97, 130.61, 127.98, 127.19, 108.60, 15.69 ppm. Anal. Found: 61.98; H, 5.39. $C_{26}H_{26}Cl_2Zr$. Anal. Calc.: C, 62.38; H, 5.23%.

2.4.1. Preparation of *5*

Reaction conditions are as follows: 4.6 ml of 1-hexyne (40 mmol), 8.6 ml of norbornadiene (80 mmol), 0.14 g of $Co_2(CO)_8$ (0.40 mmol), 30 atm of CO, and 40 ml of CH_2Cl_2. Column chromatography eluting with hexane and ethyl acetate (v/v, 10:1) gave 7.0 g of an oily product (67%). ^{1}H-NMR ($CDCl_3$): δ 7.16 (m, 1 H), 6.28 (m, 1 H), 6.20 (m, 1 H), 2.90 (s, 1 H), 2.71 (br s, 1 H), 2.66 (s, 1 H), 2.28 (d, 5.2 Hz, 1 H), 2.13 (t, 8.0 Hz, 2 H), 1.46–1.27 (m, 6 H), 0.91 (t, 7.3 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 210.42, 159.14, 151.12, 138.75, 52.89, 47.97, 43.95, 43.30, 41.52, 30.28, 25.04, 22.88, 14.24 ppm. Anal. Found: C, 82.77; H, 9.21. $C_{14}H_{18}O$ Anal. Calc.: C, 83.12; H, 8.97%.

2.4.2. Preparation of *6*

Reaction conditions are as follows: 2.9 g of *t*-butylacetylene (35 mmol), 7.6 ml of norbornadiene (70 mmol), 0.12 g of $Co_2(CO)_8$ (0.35 mmol), 30 atm of CO, and 40 ml of CH_2Cl_2. Column chromatography eluting with hexane and ethyl acetate (v/v, 10:1) gave 4.0 g of a white solid as a product (57%). ^{1}H-NMR ($CDCl_3$): δ 7.12 (m, 1 H), 6.28 (m, 1 H), 6.19 (m, 1 H), 2.89 (s, 1 H), 2.63 (m, 2 H), 2.24 (d, 5.3 Hz, 1 H), 1.33–1.17 (m, 2 H), 1.18 (s, 9 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 207.10, 156.27, 154.73, 136.43, 135.01, 51.36, 44.34, 41.81, 41.06, 38.94, 30.07, 26.28 ppm. Anal. Found: C, 83.05; H, 9.17. $C_{14}H_{18}O$ Anal. Calc.: C, 83.12; H, 8.97%.

2.4.3. Preparation of *7*

The reaction conditions are as follows: 4.7 ml of 5-hexyn-1-ol (39 mmol), 8.6 ml of norbornadiene (80 mmol), 0.14 g of $Co_2(CO)_8$ (0.40 mmol), 30 atm of CO, and 40 ml of CH_2Cl_2. Column chromatography eluting with hexane and ethyl acetate (v/v, 4:1) gave 7.6 g of an oily product (89%). ^{1}H-NMR ($CDCl_3$): δ 7.19 (m, 1 H), 6.28 (m, 1 H), 6.21 (m, 1 H), 3.68 (br s,

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **24**

	x	y	z	U_{eq} [a]
Zr1	6191(1)	10021(1)	2958(1)	65(1)
Cl1	7316(1)	10476(1)	2813(1)	78(1)
Cl2	6349(1)	8837(1)	2574(1)	94(1)
C1	5586(4)	9708(5)	3899(4)	77(2)
C2	6185(4)	9278(4)	3994(3)	72(2)
C3	6763(4)	9745(5)	4090(4)	79(2)
C4	6498(4)	10456(5)	4077(4)	81(2)
C5	5817(4)	10439(5)	3970(4)	80(2)
C6	5048(3)	10531(5)	2593(4)	76(2)
C7	5132(4)	10007(5)	2161(4)	82(2)
C8	5658(4)	10199(4)	1785(4)	72(2)
C9	5894(3)	10879(4)	2009(4)	68(2)
C10	5531(3)	11094(4)	2519(4)	71(2)
C11	4848(4)	9477(5)	3806(4)	75(2)
C12	4620(4)	8963(5)	3367(4)	85(2)
C13	3911(5)	8783(5)	3264(5)	100(3)
C14	3462(5)	9116(6)	3606(5)	106(3)
C15	3704(5)	9609(6)	4047(5)	110(3)
C16	4396(4)	9797(5)	4148(4)	95(3)
C17	6212(5)	8509(5)	4087(4)	102(3)
C18	6245(9)	8387(9)	4864(8)	188(6)
C19	6410(2)	7790(2)	4920(2)	510(3)
C20	6463(17)	8086(17)	5828(16)	425(18)
C21	7510(4)	9549(5)	4266(4)	81(2)
C22	7813(4)	9031(5)	3946(5)	99(3)
C23	8520(5)	8845(6)	4157(6)	114(3)
C24	8867(5)	9194(7)	4665(6)	112(4)
C25	8565(5)	9710(7)	4957(5)	113(4)
C26	7889(4)	9891(5)	4768(4)	90(3)
C27	5843(4)	9818(4)	1235(4)	79(2)
C28	5326(5)	9514(5)	792(5)	109(3)
C29	5491(9)	9162(7)	259(6)	142(5)
C30	6165(9)	9100(7)	161(6)	143(5)
C31	6690(7)	9355(6)	599(6)	129(4)
C32	6531(5)	9720(5)	1130(5)	103(3)
C33	6337(4)	11352(4)	1658(4)	78(2)
C34	5876(4)	11787(5)	1153(4)	92(3)
C35	6274(5)	12183(5)	715(5)	112(3)
C36	5805(6)	12619(7)	233(6)	150(4)
C37	5593(4)	11766(4)	2867(4)	73(2)
C38	6223(4)	12067(4)	3083(4)	80(2)
C39	6265(5)	12706(5)	3401(5)	99(3)
C40	5687(6)	13044(5)	3512(5)	109(3)
C41	5063(6)	12758(6)	3312(6)	117(4)
C42	5007(5)	12125(6)	2993(5)	103(3)
Zr2	1139(1)	8230(1)	2543(1)	55(1)
Cl3	1383(1)	9250(1)	3223(1)	77(1)
Cl4	2294(1)	7756(1)	2608(1)	77(1)
C51	1266(4)	8214(4)	1382(3)	67(2)
C52	1451(4)	8901(4)	1562(3)	69(2)
C53	841(4)	9242(4)	1713(3)	64(2)
C54	302(4)	8736(4)	1651(3)	63(2)
C55	573(4)	8102(4)	1435(3)	69(2)
C56	886(3)	7694(4)	3606(3)	56(2)
C57	278(3)	8003(4)	3287(3)	60(2)
C58	66(3)	7629(4)	2742(3)	59(2)
C59	542(3)	7070(4)	2682(3)	55(2)
C60	1045(3)	7117(4)	3228(3)	55(2)
C61	−440(4)	8827(4)	1733(4)	71(2)
C62	−664(4)	9208(4)	2222(4)	72(2)
C63	−1352(4)	9227(5)	2297(5)	95(3)
C64	−1820(5)	8858(7)	1900(6)	117(4)
C65	−1607(5)	8476(6)	1420(6)	120(4)
C66	−924(4)	8467(5)	1321(4)	96(3)
C67	782(4)	10008(4)	1824(4)	73(2)
C68	788(5)	10417(5)	1209(4)	100(3)
C69	796(6)	11207(5)	1313(5)	121(3)
C70	776(9)	11608(9)	667(8)	211(7)
C71	2128(4)	9227(4)	1497(4)	76(2)
C72	2416(4)	9115(5)	949(5)	98(3)
C73	3032(6)	9447(7)	862(6)	122(4)
C74	3352(6)	9875(8)	1324(7)	133(5)
C75	3088(5)	9983(6)	1870(6)	123(4)
C76	2476(5)	9652(5)	1970(5)	102(3)
C77	1229(4)	7912(4)	4250(3)	63(2)
C78	1933(4)	7962(4)	4394(4)	76(2)
C79	2222(5)	8150(5)	5003(4)	92(3)
C80	1815(6)	8298(5)	5466(4)	95(3)
C81	1114(6)	8257(5)	5321(4)	96(3)
C82	823(4)	8070(4)	4718(4)	74(2)
C83	1585(3)	6570(4)	3455(3)	63(2)
C84	1271(5)	6029(5)	3896(5)	107(3)
C85	1764(6)	5506(6)	4156(6)	141(4)
C86	1384(7)	5037(7)	4639(7)	170(5)
C87	436(3)	6514(4)	2198(3)	55(2)
C88	967(3)	6160(4)	1960(3)	62(2)
C89	851(4)	5618(4)	1529(3)	71(2)
C90	180(5)	5428(4)	1306(4)	84(2)
C91	−351(4)	5781(5)	1527(4)	90(3)
C92	−229(4)	6311(4)	1965(4)	72(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

2 H), 2.91 (s, 1 H), 2.71 (br s, 1 H), 2.67 (s, 1 H), 2.29 (m, 1 H), 2.21 (m, 2 H), 1.59 (m, 3 H), 1.37 (m, 2 H), 1.20 (d, 8.5 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 209.77, 158.99, 150.03, 138.05, 136.52, 61.65, 52.19, 47.32, 47.30, 42.55, 40.79, 31.98, 24.34, 23.76 ppm. HRMS (M^+) Calc. 218.1307, observed 218.1311.

2.5. Methylation of **7** to **8**

A total of 0.31 g of NaH (2.0 equivalents) was added 2to a solution of **7** (1.4 g, 6.6 mmol) in 15 ml of THF at r.t. under N_2. After the solution was stirred for 30 min, MeI was added. After the resulting solution was stirred for 12 h, the reaction mixture was poured into water and extracted with diethyl ether (50 ml × 2). The organic layer was separated, dried over anhydrous $MgSO_4$, concentrated, and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 4:1). After the solvent was removed, an oily product was obtained in 90% yield (1.4 g). ^{1}H-NMR ($CDCl_3$): δ 7.18 (m, 1 H), 6.28 (m, 1 H), 6.20 (m, 1 H), 3.38 (t, 6.1 Hz, 2 H), 3.33 (s, 3 H), 2.90 (s, 1 H), 2.71 (br s, 1 H), 2.66 (s, 1 H), 2.28 (d, 5.0 Hz, 1 H), 2.18 (t, 7.4 Hz, 2 H), 1.61–1.54 (m, 4 H), 1.37 (d, 9.3 Hz, 1 H), 1.20 (d, 9.3 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 210.32, 159.36,

150.75, 138.75, 137.36, 72.79, 58.96, 52.88, 48.01, 43.95, 43.27, 41.53, 29.76, 25.11, 24.70 ppm. Anal. Found: C, 77.54; H, 8.94. $C_{15}H_{20}O$ Calc.: C, 77.55; H, 8.68.

2.6. Compound **10**

To a Schlenk flask containing CuI (4.74 g, 24.9 mmol) and diethyl ether (55 ml) was added MeLi (33 ml, 1.5 M in diethyl ether solution, 50 mmol) at −20°C. The solution was stirred at −20°C for 30 min and lowered to −78°C. A solution of **5** (4.07 g, 20.1 mmol) in 10 ml of diethyl ether was added via cannula to the cold solution. The resulting solution was allowed to warm to r.t.. After the solution was stirred at r.t. for 3 h, the solution was poured into chilled water (50 ml). The mixture was filtered over celite and the etheral solution was separated. The aqueous solution was extracted with diethyl ether (50 ml). The etheral solutions were combined, dried over anhydrous $MgSO_4$, and evaporated to dryness. Chromatography of the residue on a silica gel column eluting with hexane and ethyl acetate (v/v, 5:1) gave a white solid **10** in 86% yield (3.76 g). M.p. 62–63°C. ^{1}H-NMR ($CDCl_3$): δ 6.16 (dd, 5.6, 2.9 Hz, 1 H), 6.11 (dd, 5.5, 2.9 Hz, 1 H), 3.09 (br s, 1 H), 2.75 (br s, 1 H), 2.20 (d, 8.7 Hz, 1 H), 2.02–1.98 (m, 1 H), 1.68–1.60 (m, 2 H), 1.32–1.07 (m, 5 H), 0.99 (s, 9 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 218.75, 138.72, 137.69, 69.93, 54.82, 49.17, 47.75, 45.91, 4461, 37.41, 33.13, 28.55, 25.09 ppm. HRMS (M^+) Calc. 218.1671, observed 218.1668. Anal. Found: C, 82.36; H, 10.30. $C_{15}H_{22}O$ Anal. Calc.: C, 82.52; H, 10.16%.

2.7. Compound **11**

Compound **11** was prepared by following the procedure outlined for **10** and purified by column chromatography eluting with hexane and ethyl acetate (v/v, 10:1). Yield: 85%. Oil. ^{1}H-NMR ($CDCl_3$): δ6.11 (dd, 5.6, 2.9 Hz, 1 H), 6.06 (dd, 5.6, 2.9 Hz, 1 H), 3.30 (t, 6.4 Hz, 2 H), 3.25 (s, 3 H), 3.04 (br s, 1 H), 2.67 (br s, 1 H), 2.23 (d, 9.0 Hz, 1 H), 2.22–2.05 (m, 1 H), 1.76 (t, 8.0 Hz, 1 H), 1.6–1.2 (m, 8 H), 1.16 (d, 6.5 Hz, 3 H), 1.00 (d, 9.1 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 218.10, 138.18, 137.34, 72.55, 60.55, 58.42, 54.15, 48.65, 46.58, 44.83, 44.38, 39.94, 29.90, 27.15, 23.54, 20.98 ppm. HRMS $(M+H)^+$ Calc. 249.1855, observed. 249.1857.

2.8. Compound **12**

Compound **12** was prepared by following the procedure outlined for **10** except using PhLi instead of MeLi and purified by eluting with hexane and ethyl acetate (v/v, 50:1) instead of hexane and ethyl acetate (v/v, 5:1). Yield: 83%. oil. ^{1}H-NMR ($CDCl_3$): δ 7.4–7.1 9m, 5 H), 6.15 (dd, 5.6, 2.9 Hz, 1 H), 6.08 (dd, 5.6, 2.9 Hz, 1 H), 3.21 (br s, 1 H), 2.81 9br s, 1 H), 2.86–2.76 (m, 1 H), 2.52–2.45 (m, 2 H), 2.28 (t, 8.3 Hz, 1 H), 1.7–0.9 (m, 8 H), 0.76 (t, 6.9 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 217.18, 114.68, 138.22, 137.47, 128.70, 127.99, 127.50, 126.61, 124.52, 60.59, 54.14, 52.28, 49.83, 46.60, 44.64, 44.57, 28.76, 27.14, 22.73, 13.76 ppm. HRMS (M^+) Calc. 280.1827, observed 280.1823.

2.9. Compound **13**

A U-shaped quartz tube containing 85 g of quartz chips was placed in a furnace. One of the glass joints of the quartz tube was connected to a dropping funnel containing **9** (5.40 g, 24.9 mmol) and the other joint was connected to a vacuum line via a trap which was immersed in a liquid nitrogen bath. As **9** was slowly dropped to the quartz chip bed, the product and cyclopentadiene were produced and immediately collected in a trap. After the addition was completed, the trap was connected to a aspirator to remove volatile cyclopentadiene. The remaining liquid was transferred to a flask and refluxed with 100 ml of 0.5% (w/w) KOH aqueous solution for 12 h. The product was extracted with ethyl acetate. The extracted organic solution was dried over anhydrous $MgSO_4$ and the organic solvent was removed by rotary evaporation. Product **13** was purified by vacuum distillation (55–60°C, 0.2 torr). Yield: 2.65 g (70%). ^{1}H-NMR ($CDCl_3$): δ 2.45–2.35 (m, 2 H), 2.35–2.25 (m, 2 H), 2.12 (t, 7.0 Hz, 2 H), 2.00 (s, 3 H), 1.33–1.16 (m, 4 H), 0.84 (t, 7.0 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 209.76, 170.10, 140.65, 34.25, 31.44, 30.49, 22.68, 22.63, 17.14, 13.82 ppm.

2.10. Compound **14**

Pyrolysis was done by the same method as the synthesis of **13**. However, the isomerization was done as follows. To the flask containing the pyrolyzed compound (generated by the pyrolysis of **10** (3.19 g, 14.7 mmol)) was added MeOH (50 ml) and NaOMe (0.50 g). The mixture was heated at reflux for 12 h. Vacuum distillation (35–40°C, 0.2 torr) gave the product in 50% yield. ^{1}H-NMR spectrum showed about 15% of the unisomerized compound. However, the mixture was used for further reaction without trouble. The analytically pure compound could be obtained by chromatography on a silica gel column eluting with pentane and diethyl ether (v/v, 10:1). ^{1}H-NMR ($CDCl_3$): δ 2.43–2.40 (, 2 H), 2.29–2.25 (m, 2 H), 2.20 (s, 3 H), 1.28 (s, 9 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 210.16, 167.78, 145.73, 35.34, 33.97, 33.80, 29.94, 20.08 ppm. HRMS (M^+) Calc. 152.1201, observed 152.1195.

2.11. Compound **15**

Compound **15** was prepared by using the same methodology as described above for **13**. The product was purified by vacuum distillation (80–85°C, 0.2 torr). Yield: 65%. ^{1}H-NMR ($CDCl_3$): δ 3.29 (t, 6.3 Hz, 2 H), 3.24 (s, 3 H), 2.42–2.38 (m, 2 H), 2.30–2.25 (m, 2 H), 2.12 (t, 7.4 Hz, 2 H), 1.98 (s, 3 H), 1.50–1.32 (m, 4 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 209.45, 170.22, 140.22, 72.51, 58.42, 34.18, 31.40, 29.39, 24.79, 22.63, 17.12 ppm. HRMS (M^+) Calc. 182.1307, observed 182.1305.

2.12. Compound **16**

A quartz tube containing **12** (1.127 g, 4.0 mmol) was connected via a flexible tube to a Schlenk flask. After the system was purged with argon, the quartz tube was placed into a furnace whose temperature has been set at 420°C and the Schlenk flask was immersed in liquid nitrogen bath. After 5 min, the quartz tube was removed from the furnace and was cooled to r.t.. Purification of the crude product was carried out by chromatography on a silica gel column eluting with hexane and ethyl acetate (v/v, 10:1). Yield: 0.58 g (67%). ^{1}H-NMR ($CDCl_3$): δ 7.45–7.26, 2.88–2.83 (m, 2 H), 2.51–2.46 (m, 2 H), 2.35 (t, 7.8 Hz, 2 H), 1.48–1.22 (m, 4 H), 0.85 (t, 7.2 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 209.66, 166.96, 141.25, 136.69, 129.21, 128.58, 127.12, 34.19, 30.38, 29.77, 23.75, 22.89, 13.75 ppm. HRMS (M^+) Calc. 214.1358, observed 214.1356.

2.13. Compound **17**

To a Schlenk flask containing **13** (0.607 g, 3.99 mmol) in 10 ml of Et_2O at -78 °C was added MeLi (4.0 ml, 1.5 M in Et_2O, 6.0 mmol). The solution was allowed to warm to r.t.. After the solution was stirred for 5 h, 10 ml of water was added. Diethyl ether was removed by rotary evaporator while keeping the bath temperature below 25°C. Ethyl acetate (40 ml) was added to the residue. The mixture was poured into a separating funnel. The aqueous layer was removed and aqueous 2 N HCl solution (40 ml) was added. The separating funnel was vigorously shaken for 3 min. The aqueous layer was removed and the organic layer was washed with concentrated aqueous $NaHCO_3$ solution (30 ml). The organic layer was collected and dried over anhydrous $MgSO_4$. After removal of the solvent by rotary evaporator while keeping the bath temperature at 0°C, the residue was purified by column chromatography on a short (5 cm) silica gel eluting with pentane. Yield: 0.50 g (85%). Since this compound was obtained as an 8:1 mixture with the isomerized product, the corresponding signals are also present in the ^{1}H-NMR spectrum. These peaks are omitted from the following list. ^{1}H-NMR ($CDCl_3$): δ 5.81 (s, 1 H), 2.76 (s, 2 H), 2.23 (t, 7.0 Hz, 2 H), 1.93 (s, 6 H), 1.4–1.3 (m, 4 H), 0.92 (t, 6.7 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.86, 140.46, 136.90, 123.61, 43.74, 32.10, 25.43, 22.81, 14.29, 14.07, 13.75 ppm. HRMS $(M+H)^+$ Calc. 151.1487, observed. 151.1478.

2.14. Compound **18**

Compound **18** was prepared by using the same methodology as described above for **17**. Purification of the crude product was done by chromatography on a silica gel column eluting with hexane and ethyl acetate (v/v, 10:1). No side product was found. Yield: 76%. ^{1}H-NMR ($CDCl_3$): δ 5.82 (s, 1 H), 2.73 (br s, 2 H), 2.11 (d, 1.7 Hz, 3 H), 2.10 (s, 3 H), 1.29 (s, 9 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 145.29, 135.73, 126.93, 46.41, 34.76, 31.30, 19.09, 17.20 ppm. HRMS $(M+H)^+$ Calc. 151.1487, observed 151.1480.

2.15. Compound **19**

Compound **19** was prepared by using the same methodology as described above for **17**. Purification of the crude product was done by chromatography on a silica gel column eluting with hexane and ethyl acetate (v/v, 10:1). Product was obtained as an 8:1 mixture with the isomerized product. Yield: 84%. ^{1}H-NMR ($CDCl_3$): δ 5.79 (s, 1 H), 3.36 (t, 6.5 Hz, 2 H), 3.30 (s, 3 H), 2.73 (s, 2 H), 2.45 (t, 7.6 Hz, 2 H), 1.91 (s, 6 H), 1.60–1.40 (m, 4 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.58, 139.94, 137.15, 123.62, 72.76, 58.45, 43.66, 29.52, 26.20, 25.31, 14.18, 13.71 ppm. HRMS $(M+H)^+$ Calc. 181.1592, observed 181.1578.

2.16. Compound **20**

Compound **20** was prepared by using the same methodology as described above for **17**. PhLi was used instead of MeLi. Dehydration was done by shaking with 6 N HCl solution for 10 min instead of shaking with 2 N HCl solution for 3 min. Purification of the crude product was done by chromatography on a silica gel column eluting with hexane and ethyl acetate (v/v, 40:1). Yield: 86%. ^{1}H-NMR ($CDCl_3$): δ7.4–7.2 (m, 10 H), 6.34 (s, 1 H), 3.39 (s, 2 H), 2.58 (t, 7.0 Hz, 2 H), 1.2–1.1 (m, 4 H), 0.67 (t, 7.0 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 150.00, 142.02, 141.20, 138.15, 129.41, 128.12, 127.96, 127.90, 126.88, 1267.15, 43.30, 31.22, 26.18, 22.54, 13.59 ppm. HRMS (M^+) Calc. 274.1722, observed 274.1718.

2.17. Compound **21**

To a Schlenk flask containing **17** (0.302 g, 2.04 mmol) in 10 ml of THF at −78 °C was added *n*-BuLi (0.82 ml, 2.5 M in hexane, 2.1 mmol). The solution was allowed to warm to r.t. After the solution was stirred for 4 h, solid $ZrCl_4(THF)_2$ (0.38 g, 1.0 mmol) was added. The mixture was stirred at 60°C for 40 h. After removal of the solvent, the residue was treated with hot anhydrous hexane. The hot filtered hexane solution was kept in a freezer (ca. −30°C) for 1 day. Solids were deposited, collected by removing the hexane solution, and dried in a vacuum. Yield: 0.32 g (70%). White solid, M.p. 169–170°C. ^{1}H-NMR ($CDCl_3$): δ 5.79 (s, 2 H), 2.44 (t, 7.6 Hz, 2 H), 2.04 (s, 6 H), 1.37–1.30 (m, 4 H), 0.89 (t, 7.0 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 131.32, 128.75, 108.28, 31.61, 26.08, 22.88, 14.54, 14.01 ppm. HRMS (M^+) Calc. 458.1085, observed 458.1082. Anal. Found: C, 57.35; H, 7.28. $C_{22}H_{34}Cl_2Zr$ Anal. Calc.: C, 57.36; H, 7.44%.

2.18. Compound **22**

Compound **22** was prepared by using the same methodology as described above for **21**. Yield: 69%. White solid. M.p. 193–194°C. ^{1}H-NMR ($CDCl_3$): δ 5.68 (s, 2 H), 2.67 (s, 6 H), 1.37 (s, 9 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 136.47, 131.11, 110.45, 35.97, 31.12, 19.21 ppm. Anal. Found: 56.94; H, 7.09. $C_{22}H_{34}Cl_2Zr$ Anal. Calc.: C, 57.36; H, 7.44%.

2.19. Compound **23**

Compound **23** was prepared by using the same methodology as described above for **21**. Yield: 85%. White solid. M.p. 101–102°C; ^{1}H-NMR ($CDCl_3$): δ 5.79 (s, 2 H0, 3.35 (t, 6.4 Hz, 2 H), 3.29 (s, 3 H), 2.46 (t, 7.8 Hz, 2 H), 2.03 (s, 6 H), 1.6–1.4 (m, 4 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 130.89, 128.88, 108.29, 75.52, 58.58, 29.67, 26.02, 25.92, 14.56 ppm. HRMS $(M+H)^+$, Calc. 519.1374, observed 519.1368. Anal. Found: 55.23; H, 6.83. $C_{24}H_{38}Cl_2O_2Zr$ Anal. Calc.: C, 55.36; H, 7.36%.

2.20. Compound **24**

Compound **24** was prepared by using the same methodology as described above for compound **20**. Yield: 73%. Light yellow solid. M.p. 151–152°C. ^{1}H-NMR ($CDCl_3$): δ 7.44–7.20 (m, 10 H), 5.76 (s, 2 H), 2.90 (t, 7.0 Hz, 2 H), 0.89–0.76 (m, 4 H), 0.41 (t, 7.1 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 136.59, 135.12, 129.02, 128.54, 127.82, 127.53, 113.78, 30.37, 26.29, 22.02, 13.35 ppm. Anal. Found: C, 71.43; H, 5.75. $C_{42}H_{42}Cl_2Zr$ Anal. Calc.: C, 71.16; H, 5.97%.

2.21. X-ray crystal structure determination of **24**

Single crystals of **24** suitable for X-ray structure determination were grown in a hexane solution of **24** at −30°C. A yellow crystal of **24**, shaped as a block of approximate dimensions $0.42 \times 0.40 \times 0.32$ mm, was used for crystal and intensity data collection. Data were collected on a Siemens P4 diffractometer with Mo–K_α radiation (graphite monochromator). Details of the crystal and intensity data are given in Table 1. The intensities were corrected for Lorentz and polarization effects. The structure was solved by the heavy atom method and refined against F^2 by full-matrix least-squares with the SHELXYL program, initially isotropic and finally anisotropic temperature factors for all non-hydrogen atoms except the carbons in the butyl groups. The anisotropic refinements including the carbon atoms in the butyl groups were unstable and therefore they (C17 − C19, C33–C36, C67–C70, and C83–C86) were isotropically refined. All hydrogen atoms were generated in idealized positions and refined using a riding model. Tables of complete bond lengths and angles, anisotropic displacement parameters, and hydrogen atom positional and displacement parameters for **24** are available from the authors.

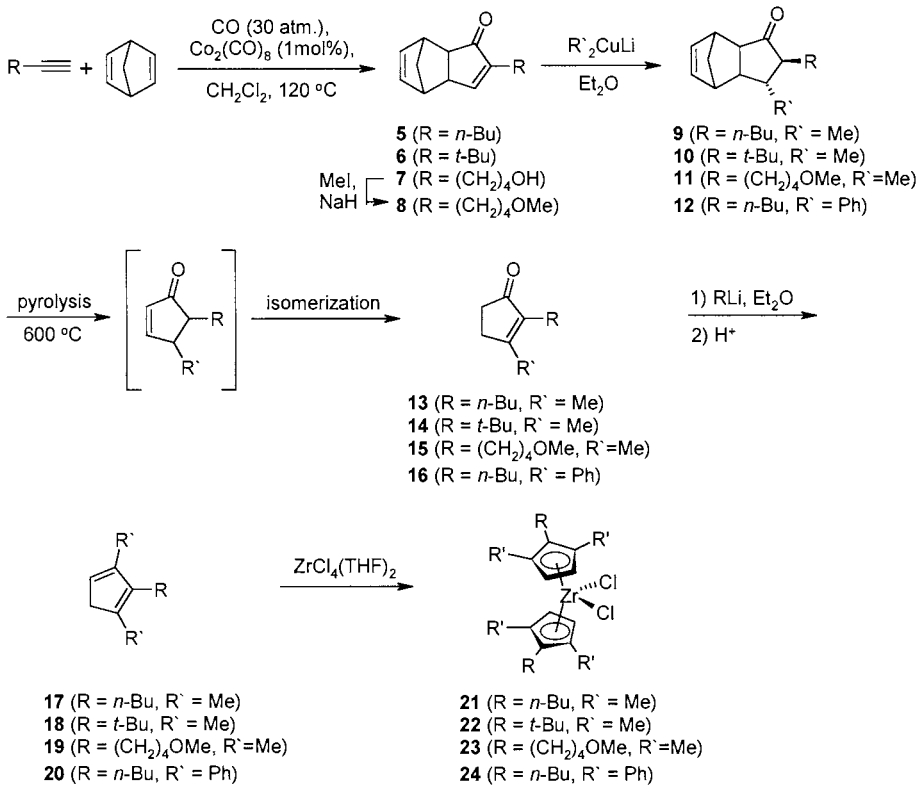
2.22. Polymerization of ethylene

To a dried 500 ml glass reactor was added hexane (200 ml). The solution was degassed by ethylene. After the reactor was immersed in an oil bath (80°C) for 15 min, the preactivated catalyst (prepared by mixing of MAO (1.4 ml, 2.9 mmol Al, 6.4 w% Al in toluene) with zirconocene complex (0.5 μmol) in 10 ml of toluene for 15 min at room temperature) was added via syringe. While the solution was stirring, ethylene was fed continuously under a pressure of 40 psig for 15 min. The reaction was quenched by addition of 5 ml of MeOH. After the solution was filtered, polymers were obtained and dried under vacuum at 80°C. For comparison, bis(cyclopentadienyl)zirconium dichloride was also studied.

3. Results and discussion

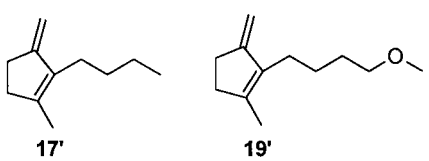
3.1. Synthesis of catalyst precursors

The precursors **1** and **2** were prepared by the known procedures (Scheme 1) [6]. To use the reaction procedures in Scheme 1, the presence of one phenyl group was required. Complexes **3** and **4** were prepared by deprotonation of **1** and **2** in THF followed by addition of 0.5 equivalents of $ZrCl_4(THF)_2$ in the same solvent. Crystallization of the products from toluene or toluene and hexane gave **3** and **4** in 54% yield, respectively.



Scheme 2.

Other precursors were prepared by the general procedures in Scheme 2. The catalytic intermolecular Pauson–Khand reaction [9] between norbornadiene and appropriately substituted alkynes afforded cyclopentenone derivatives **5**–**7**. Compound **8** was prepared by methylation of **7** [6]. Nucleophilic 1,4-addition of R'_2CuLi ($R' = Me$, Ph) [7] to **5**, **6**, and **8** led to isolation of **9**–**12** in 83–86% yields. Compound **9** was previously reported by Schore [10]. Pyrolysis of **9**–**12** and isomerization [11] of the pyrolyzed products gave compounds **13**–**16** in 50–70% yields. Nucleophilic addition of R′Li to **13**–**16** and followed by dehydration yielded **17**–**20** in 76–86% yields. Interestingly, treatment of 4,5-disubstituted cyclopentenones with MeLi and followed by dehydration did not give the corresponding dehydrated products. Thus, the isomerization step is prerequisite to perform a dehydration reaction. One notable thing is that treatment of **17** and **19** were obtained with a small amount of side products, presumably **17′** and **19′** by ^{1}H-NMR.



17' **19'**

The trisubstituted cyclopentadiene was deprotonated with 1 equivalent of butyl-lithium in THF, and 0.5 equivalents of $ZrCl_4(THF)_2$ was added in the same solvent. Recrystallization of the complexes from hexane gave **21**–**24** in 69–73% yield.

When we follow the reaction sequences in Scheme 1, the 1,4–nucleophilic addition and isomerization steps in Scheme 2 can be skipped. Thus, it seems that the reaction sequences in Scheme 1 are more convenient than those in Scheme 2. However, to use the reaction sequences in Scheme 1, in many cases we have to synthesize internal alkynes in laboratories. However, when we use the reaction sequences in Scheme 2, most of the terminal alkynes are commercially available or easily synthesized. Furthermore, terminal alkynes can be effectively transformed to the corresponding cyclopentenones with norbornadiene by the catalytic reaction while the internal alkynes are sluggish in the catalytic reaction [12]. Thus, Scheme 2 seems to be a more general and effective reaction scheme. Furthermore, to synthesize **20**, the reaction sequences in Scheme 1 cannot be applicable due to the regioselectivity of the Pauson–Khand reaction. Thus, Schemes 1 and 2 can complement each other.

3.2. X-ray crystal structure of **24**

There are two crystallographically independent molecules in the asymmetric unit. One of the two molecular structures of **24** with the atomic numbering scheme is shown in Fig. 1. The two molecules are chemically equivalent. Details on the crystal and intensity data are given in Table 1 and the fractional atomic coordinates appear in Table 2. The molecules have a pseudo 2-fold (C_2) axis running Zr2 and the two Cp rings are approximately in eclipsed conformation where the substituents on the Cp rings are on the cross way to each other to reduce the steric congestion. Due to the steric bulkiness of the substituents on the Cp rings, the angle (99.06(7)°) between Cl3–Zr–Cl4 is relatively wide. The steric interaction between substituents on the Cp ring leads to the lengthening of the C–C bonds connecting the two phenyl rings and the butyl group. Thus, the bond distances of C52–C53, C53–C54 and C53–C54 are longer than those of C51–C52 and C51–C55. The bond distances (2.230 and 2.226 Å) of Cpcent–Zr and angle (130.8°) between Cpcent–Zr–Cpcent in **24** are similar to those found in bis-(2-phenylindenyl)zirconium dichlorides [13] and bis(indenyl)zirconium dichloride [14].

3.3. Polymerization results

Precursors were activated with MAO and used to polymerize ethylene. Gaseous ethylene (40 psig pressure) reacts with the activated complexes of **3**, **4**, and **21**–**24** with MAO in hexane under vigorously anhydrous, anaerobic conditions. Cp_2ZrCl_2 was studied to compare the activity. The activity of the catalysts and the molecular weight distribution of the produced polymer are shown in Table 3 The yields (Table 3), as determined by quenching the polymerization reactions (addition of MeOH) after a measured time interval (15 min), suggest that the activities of complexes **4** and **21** are higher than that of Cp_2ZrCl_2 under similar conditions. The activity of **21** containing two methyl groups and one *n*-butyl group was almost four times higher than that of Cp_2ZrCl_2. Compounds **22** and **23** showed similar activities to Cp_2ZrCl_2. However, two or three phenyl substitution as in **3** and **24** exhibit negligible activities, presumably due to the steric effect of phenyl groups. When we compare the polymerization activities for **3**, **4**, **21**–**24**, and Cp_2ZrCl_2, the order is **21** > **4** > **22** ~ **23** ~ Cp_2ZrCl_2 > **3** ~ **24**. Thus, substitution by phenyl, *n*-butyl, *t*-butyl, and $(CH_2)_4OCH_3$ on the C-2 position of the Cp ring leads to a catalyst with decreasing activity in the order of *n*-Bu > Ph > $(CH_2)_4OCH_3$ > *t*-Bu. The relatively low activity of **23** having $(CH_2)_4OCH_3$ might be due to the coordination of the oxygen atom to the metal center [15]. The *t*-butyl group reduced the activity and molecular weight of the polymer. Significant reduction of activity and molecular weight by introduction of a *t*-butyl group in the cyclopentadienyl ligand was also reported [16].

Table 3
Results of the polymerization of ethylene

Compound	Yield (g)	Mw ($\times 10^{+3}$)	Mw/Mn
4	4.1	269	2.4
21	6.0	319	2.3
22	1.9	37	2.3
23	1.5	369	3.4
Cp_2ZrCl_2	1.5	110	2

Molecular weights and molecular weight distributions of the polymers were determined by GPC analysis. As shown in Table 3, **4**, **21**, and **23** produced polymers with higher molecular weights than Cp_2ZrCl_2. The order of the molecular weight with the variation of the substituent on C-2 was $(CH_2)_4OCH_3$ > *n*-Bu > Ph > *t*-Bu. While the molecular weight distribution (Mw/Mn = 2.3–2.4) of the polymers obtained by catalysts **4**, **21**, **22** showed a characteristic feature of the single site catalyst, **23** having an ether bond produced polymers of rather broad molecular weight distribution (Mw/Mn = 3.4) [15].

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