



# Preparation of titanocene and zirconocene dichlorides bearing bulky 1,4-dimethyl-2,3-diphenylcyclopentadienyl ligand and their behavior in polymerization of ethylene

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## ABSTRACT

New metallocene dichlorides [ $\eta^5$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>-C<sub>5</sub>H)<sub>2</sub>TiCl<sub>2</sub>] (**2**), [ $\eta^5$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>-C<sub>5</sub>H)<sub>2</sub>ZrCl<sub>2</sub>] (**3**) and [ $\eta^5$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>-C<sub>5</sub>H) $\eta^5$ -(C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>2</sub>] (**4**) were prepared from lithium salt of 1,4-dimethyl-2,3-diphenylcyclopentadiene (**1**) and [TiCl<sub>3</sub>(THF)<sub>3</sub>], [ZrCl<sub>4</sub>] and [ $\eta^5$ -(C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub>(DME)], respectively. Compounds **2–4** were characterized by NMR spectroscopy, EI-MS and IR spectroscopy, and the solid state structure of **3** was determined by single crystal X-ray crystallography. The catalytic systems **3**/MAO and **4**/MAO were almost inactive in polymerization of ethylene at 30–50 °C, however, they exhibited high activity at temperature 80 °C. The catalyst formed from **2** and excess of MAO was practically inactive at all temperatures.

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## 1. Introduction

Highly substituted cyclopentadienes as ligands for group 4 metallocene complexes are still one of the important subjects of organometallic chemistry. Apart from complexes bearing persubstituted bulky cyclopentadienes [1], which were extensively studied in past decades, examples of complexes with relatively bulky phenyl substituted cyclopentadienyl rings still remain rather rare.

Complexes containing the substituted cyclopentadienyl ligand of general formula (1,2-Ph<sub>2</sub>-4-R-C<sub>5</sub>H<sub>2</sub>) became exploited after the first zirconocene dichlorides with R = H in their ligands were developed [2]. Molecular orbitals of [ $\eta^5$ -(1,2-Ph<sub>2</sub>-4-R-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub>] (where R = H, Me, Ph) were calculated by DFT method and the theoretical and experimental UV spectra were compared [3]. Monocyclopentadienyl titanium trichlorides with the ligand 1,2-Ph<sub>2</sub>-4-R-C<sub>5</sub>H<sub>2</sub> (where R = Me, Bu, Ph) after activation with MAO (MAO – methylaluminoxane) afforded syndiotactic polystyrene with high productivity and selectivity [4,5]. Very recently, the constrained geometry complex [ $\eta^5$ -(1,2-Ph<sub>2</sub>-C<sub>5</sub>H<sub>3</sub>)(SiMe<sub>2</sub>N-tBu)-TiMe<sub>2</sub>] developed by Arriola et al. showed a high activity in

ethylene-styrene copolymerization with substantially increased ratio of styrene units in the resulting resin compared to other catalytic systems [6].

Coming from our permanent interest in group 4 metallocene dichlorides bearing phenyl substituted cyclopentadienyl ligand [7] we have investigated the cyclopentadienyl ligand having two methyl groups in 1,4- positions in addition to two vicinal phenyl groups (i.e. 1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>-C<sub>5</sub>H). Although the parent 1,4-dimethyl-2,3-diphenylcyclopentadiene is known for more than 40 years, its utilization as a ligand in organometallic chemistry has been so far limited to only one example [8,9].

Here, we report the preparation and characterization of titanium and zirconium complexes containing 1,4-dimethyl-2,3-diphenylcyclopentadienyl ligand and the catalytic behavior of catalysts prepared thereof in polymerization of ethylene.

## 2. Experimental

### 2.1. Materials and equipments

All reactions with moisture- and air-sensitive compounds were carried out under argon (99.999%) or nitrogen (Siad 99.999%) atmosphere using standard Schlenk techniques. Solvents were dried, and freshly distilled prior to use. ZrCl<sub>4</sub> and *n*-butyllithium (1.6 M) were obtained from Aldrich and used as received.

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[TiCl<sub>3</sub>(THF)<sub>3</sub>] [10] (THF – tetrahydrofuran) and [ $\eta^5$ -(C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub>-(DME)] [11] (DME – dimethoxyethane) were prepared according to literature procedures.

Ethylene (Siad 99.5%) for polymerization experiments was purified by passing through columns with copper catalyst and molecular sieves to remove traces of oxygen and moisture. Metallocene precatalysts were used as toluene solutions, which were stored in Schlenk vessels at 5 °C. MAO (Crompton, 10% in toluene) was used as received.

1,4-Dimethyl-2,3-diphenylcyclopentadiene was prepared following a published procedure and characterized by spectroscopic data which were missing in [8]. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz) were measured on a Bruker DRX500 spectrometer in C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub> solution at 300 K. Chemical shifts are given relative to the solvent signal ( $\delta_H$  7.15 ppm,  $\delta_C$  128.00 ppm for C<sub>6</sub>D<sub>6</sub> and  $\delta_H$  7.26 ppm,  $\delta_C$  77.16 ppm for CDCl<sub>3</sub>). Mass spectra were measured on a KRATOS concept IS instrument (Centre de Spectroscopie Moléculaire de l'Université de Bourgogne) at 70 eV. Infrared spectra were recorded on a Nicolet Avatar FT IR spectrometer in the range 400–4000 cm<sup>-1</sup>. Melting points of organic compounds and complexes were measured on Koffler block and were uncorrected. Elemental analyses (EA) were carried out on an Elementar vario EL III facility (Elementar) and average values from at least two measurements were taken. The polyethylene melting temperature was determined by DSC (TA Instruments, Q100) from the second heating run using heating and cooling rate 10 °C min<sup>-1</sup>. Molar masses of polyethylenes were determined by viscometry in decaline at 135 °C using Mark-Houwink parameters  $K = 6.2 \times 10^{-4}$  and  $a = 0.70$  [12].

## 2.2. Characterization of 1,4-dimethyl-2,3-diphenylcyclopenta-1,3-diene (**1**) [8]

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 1.94 (s, 6H, Me); 2.74 (s, 2H, CH<sub>2</sub>), 6.97–7.01 (m, 2H, CH<sub>para</sub>, Ph), 7.05–7.12 (m, 8H, CH, Ph). <sup>13</sup>C{<sup>1</sup>H}(C<sub>6</sub>D<sub>6</sub>): 14.43 (Me); 49.90 (CH<sub>2</sub>); 126.37, 128.02, 129.92 (CH, Ph); 136.19, 137.24, 142.19 (C<sub>q</sub>; C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub> and Ph). EI-MS (70 °C): *m/z* (relative abundance) 247 (25), 246 (M<sup>+</sup>; 100), 231 ([M–Me]<sup>+</sup>; 16), 216 ([M–2Me]<sup>+</sup>; 14), 215 (22), 202 (9), 165 (5), 155 (6), 153 (6), 152 (6), 128 (4), 115 (6), 91 (3), 77 (2). IR (KBr, cm<sup>-1</sup>): 3100 (vw), 3076 (s), 3050 (m), 3028 (w), 2980 (w), 2969 (w), 2939 (w), 2902 (s), 2849 (m), 2731 (vw), 1955 (vw), 1888 (vw), 1816 (vw), 1767 (vw), 1602 (s), 1570 (w), 1494 (s), 1484 (m), 1440 (vs), 1373 (s), 1308 (w), 1240 (w), 1228 (vw), 1179 (vw), 1154 (w), 1128 (vw), 1076 (m), 1031 (vw), 1014 (vw), 1004 (w), 983 (m), 923 (w), 834 (vw), 772 (s), 756 (vs), 707 (vs), 683 (w), 646 (w), 620 (vw), 567 (m), 501 (vw), 433 (vw).

## 2.3. Preparation of bis( $\eta^5$ -1,4-dimethyl-2,3-diphenylcyclopentadienyl)titanocene dichloride (**2**)

A 1.6 M *n*-butyllithium in hexane (4.5 ml, 7.19 mmol) was added dropwise to a solution of **1** (1.77 g, 7.19 mmol) in diethyl ether (80 ml) cooled to 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred overnight. The resulting pale beige precipitate was filtered, washed three times with 20 ml of diethyl ether and dried in vacuum. A beige powder of lithium salt of **1** (1.65 g, 6.54 mmol) was dissolved in THF to give a the deep red solution. This was cooled to –78 °C, and [TiCl<sub>3</sub>(THF)<sub>3</sub>] (1.21 g, 3.27 mmol) was gradually added under stirring. The reaction mixture was allowed to warm to room temperature, and then refluxed for 12 h. The resulting dark green mixture was cooled to room temperature, and carbon tetrachloride (2.0 ml) was added. This caused an immediate color change to deep brown. After reflux for 2 h, all volatiles were evaporated to vacuum, the solid residue

was dissolved in 60 ml of toluene, and filtered through cellite pad. The volume of a dark brown toluene extract was concentrated to ca. 15 ml and stored at –18 °C for several days. Dark brown microcrystals were isolated, washed with cold toluene (5 ml), hexane (3 × 10 ml) and dried in vacuum. Yield 1.12 g (56%).

M.p. 235 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 2.06 (s, 6H, Me); 2.10 (s, 1.5H, PhMe<sup>\*</sup>); 5.77 (s, 1H, CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 6.93–6.98 (m, 2H, CH<sub>para</sub>, Ph); 6.99–7.02 (m, 1.5H, PhMe<sup>\*</sup>); 7.03–7.07 (m, 4H, CH<sub>ortho</sub>, Ph); 7.10–7.15 (m, 1H, PhMe<sup>\*</sup>); 7.42–7.47 (m, 4H, CH<sub>meta</sub>, Ph). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.38 (s, 6H, Me); 2.43 (s, 1.5H, PhMe<sup>\*</sup>); 6.41 (s, 1H, CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 7.22–7.36 (m, 10H + 2.5H<sup>\*</sup>, CH, C<sub>5</sub>Ph and PhMe<sup>\*</sup>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>): 17.15 (C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>); 21.61 (PhMe<sup>\*</sup>); 116.98 (CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 125.44, 128.37, 129.18 (CH, PhMe<sup>\*</sup>); 127.30, 127.40, 132.08 (CH, C<sub>5</sub>Ph); 125.25, 134.12, 139.27 (C<sub>q</sub>; C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H and Ph) 138.02 (C<sub>q</sub>; PhMe<sup>\*</sup>). Signals denoted by asterisk belong to half equivalent of solvating toluene. EI-MS (200 °C): *m/z* (relative abundance) 610 (12), 609 (8), 608 (M<sup>+</sup>; 17), 573 ([M–Cl]<sup>+</sup>; 47), 400 (10), 399 (8), 365 (78), 364 (33), 363 ([M–C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 100), 328 ([M–C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H–Cl]<sup>+</sup>; 22), 327 (21), 326 (14), 325 (27), 246 (62), 245 ([C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 88), 230 ([C<sub>5</sub>MePh<sub>2</sub>H]<sup>+</sup>; 27), 229 (35), 228 (25), 215 ([C<sub>5</sub>Ph<sub>2</sub>H]<sup>+</sup>; 49), 167 (14), 165 (12), 152 (11), 129 (7), 128 (5), 115 (9), 91 (22). IR (KBr, cm<sup>-1</sup>): 3087 (m), 3055 (s), 3026 (s), 2957 (m), 2917 (s), 1601 (m), 1575 (w), 1505 (w), 1494 (m), 1486 (m), 1463 (s), 1439 (s), 1422 (m), 1381 (m), 1366 (m), 1324 (vw), 1283 (vw), 1237 (vw), 1183 (w), 1156 (vw), 1079 (w), 1019 (m), 1002 (vw), 981 (vw), 919 (vw), 868 (w), 767 (s), 753 (vs), 731 (s), 698 (vs), 644 (w), 624 (m), 613 (w), 572 (vw), 506 (w), 465 (w). EA for C<sub>38</sub>H<sub>34</sub>Cl<sub>2</sub>Ti · 1/2 C<sub>7</sub>H<sub>8</sub> (655.55) calcd. C 76.04, H 5.84%; found C 75.49, H 5.95%.

## 2.4. Preparation of bis( $\eta^5$ -1,4-dimethyl-2,3-diphenylcyclopentadienyl)zirconocene dichloride (**3**)

A 1.6 M *n*-butyllithium in hexane (13.4 ml, 21.4 mmol) was added dropwise to a stirred solution of **1** (5.27 g, 21.4 mmol) in toluene (60 ml). The reaction mixture with the precipitated lithium salt of **1** was stirred for 5 h, and ZrCl<sub>4</sub> (2.50 g, 10.7 mmol) was added in one portion. The resulting suspension was stirred for 1 h at ambient temperature and then refluxed for 2 days. The volatiles were evaporated and the residue was heated to 170 °C in vacuum for 4 h to remove traces of unreacted **1**. The resulting yellow-brown solid was extracted in Soxhlet extractor with boiling hexane within 2 days. The yellow solid which precipitated during extraction from the hexane solution was isolated, washed with hexane (3 × 15 ml), ethanol (3 × 15 ml), and dried in vacuum. Yield 2.06 g (30%).

M.p. 264 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 2.10 (s, 6H, Me); 5.69 (s, 1H, CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 6.91–6.98 (m, 2H, CH<sub>para</sub>, Ph); 7.01–7.09 (m, 4H, CH<sub>ortho</sub>, Ph); 7.40–7.45 (m, 4H, CH<sub>meta</sub>, Ph). <sup>13</sup>C{<sup>1</sup>H}(C<sub>6</sub>D<sub>6</sub>): 16.05 (Me); 114.02 (CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 127.35, 127.88, 132.06 (CH, Ph); 122.01, 134.31, 134.43 (C<sub>q</sub>; C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H and Ph). EI-MS (210 °C): *m/z* (relative abundance) 654 (9), 653 (6), 652 (M<sup>+</sup>; 11), 651 (7), 650 (10), 411 (50), 410 (25), 409 (97), 408 (51), 407 ([M–C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 100), 406 (61), 405 (99), 393 (16), 392 (8), 391 (23), 390 (15), 389 (31), 373 (28), 371 (19), 370 (12), 369 (30), 368 (12), 367 (24), 365 (12), 246 (39), 245 ([C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 18), 244 (14), 230 ([C<sub>5</sub>MePh<sub>2</sub>H]<sup>+</sup>; 14), 229 (28), 228 (20), 216 (13), 215 ([C<sub>5</sub>Ph<sub>2</sub>H]<sup>+</sup>; 27), 167 (11), 165 (13), 152 (12), 115 (16), 91 (19), 77 (10). IR (KBr, cm<sup>-1</sup>): 3089 (m), 3051 (m), 2988 (w), 2955 (m), 2923 (m), 1601 (m), 1576 (w), 1506 (m), 1485 (w), 1462 (m), 1441 (s), 1381 (w), 1322 (vw), 1311 (vw), 1283 (vw), 1238 (vw), 1184 (w), 1157 (vw), 1079 (w), 1032 (w), 1017 (w), 1003 (vw), 983 (vw), 920 (vw), 863 (vw), 844 (m), 767 (s), 753 (vs), 699 (vs), 645 (w), 626 (m), 614 (w), 571 (w), 506 (vw), 416 (vw). EA for C<sub>38</sub>H<sub>34</sub>Cl<sub>2</sub>Zr (652.82) calcd. C 69.92, H 5.25%; found C 69.64, H 5.36%.

## 2.5. Preparation of ( $\eta^5$ -cyclopentadienyl)( $\eta^5$ -1,4-dimethyl-2,3-diphenylcyclopentadienyl)zirconocene dichloride (**4**)

A mixture of solid lithium salt of **1** (prepared as for **2**) (0.36 g, 1.42 mmol) and [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>2</sub>(DME)] (0.50 g, 1.42 mmol) was cooled to  $-78^\circ\text{C}$  and 20 ml of toluene was added. The reaction mixture was stirred for 10 min at this temperature, then allowed to warm to room temperature, and refluxed for 2 days. The resulting greenish suspension was filtered through a cellulose pad. The resulting yellow filtrate was concentrated to ca. 8 ml and stored in a freezer ( $-18^\circ\text{C}$ ) for several days. Yellowish microcrystals were collected, washed with cold toluene (5 ml), hexane ( $3 \times 5$  ml), and dried in vacuum. Yield 0.26 g (39%).

M.p. 164–165  $^\circ\text{C}$ .  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>): 2.01 (s, 6H, Me); 5.42 (s, 1H, CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 5.98 (s, 5H, CH, C<sub>5</sub>H<sub>5</sub>); 6.94–6.99 (m, 2H, CH<sub>para</sub>, Ph); 7.02–7.07 (m, 4H, CH<sub>ortho</sub>, Ph); 7.30–7.34 (m, 4H, CH<sub>meta</sub>, Ph).  $^{13}\text{C}\{^1\text{H}\}$ (C<sub>6</sub>D<sub>6</sub>): 15.97 (Me); 115.22 (CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 116.51 (CH, C<sub>5</sub>H<sub>5</sub>); 127.40, 128.04, 131.54 (CH, Ph); 124.24, 131.49, 134.04 (C<sub>q</sub>; C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H and Ph). EI-MS (210  $^\circ\text{C}$ ):  $m/z$  (relative abundance) 474 (20), 473 (12), 472 (M<sup>+</sup>; 28), 471 (14), 470 (27), 435 ([M-Cl]<sup>+</sup>; 5), 411 (33), 410 (18), 409 (71), 408 (36), 407 ([M-C<sub>5</sub>H<sub>5</sub>]<sup>+</sup>; 99), 406 (43), 405 (100), 391 (12), 389 (16), 371 (13), 369 (22), 367 (19), 365 (11), 246 (15), 245 ([C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 8), 244 (9), 229 (21), 228 (17), 227 ([M-C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 16), 225 (16), 215 (22), 202 (11), 165 (11), 152 (11), 128 (11), 115 (14), 91 (15), 77 (11). IR (KBr, cm<sup>-1</sup>): 3112 (m), 3089 (m), 3060 (m), 2989 (w), 2956 (w), 2929 (w), 1601 (w), 1576 (vw), 1505 (w), 1485 (w), 1464 (w), 1441 (s), 1380 (w), 1314 (vw), 1239 (vw), 1185 (vw), 1157 (vw), 1127 (vw), 1077 (w), 1016 (m), 1003 (vw), 986 (vw), 919 (vw), 819 (vs), 766 (s), 754 (s), 701 (vs), 669 (w), 654 (w), 628 (w), 615 (w), 572 (w), 508 (w), 418 (w). EA for C<sub>24</sub>H<sub>22</sub>Cl<sub>2</sub>Zr (472.57) calcd. C 61.00, H 4.69%; found C 60.62, H 4.52%.

## 2.6. X-ray crystallography

The yellow-green crystal of **3** was grown from its dichloromethane solution during hexane diffusion. Diffraction data were collected on a Nonius KappaCCD diffractometer. The structure was solved by direct methods (SIR-97) [13] and refined by weighted full-matrix least-squares on  $F^2$  (SHELXL-97) [14]. All non hydrogen

atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in calculated positions. Relevant crystallographic data are collected in Table 1.

## 2.7. Ethylene polymerization

Polymerizations were carried out in 100 ml magnetically stirred jacket glass reactor. Toluene, ethylene and MAO solution were dosed in this order and the mixture was stirred for 15 min to equilibrate reaction temperature. The polymerization was started by injection of the precatalyst solution. The ethylene pressure was kept constant (1.1 atm) during the whole polymerization. The polymerization was quenched by 2 ml of EtOH/HCl mixture and polymer precipitated in a large excess of 3% HCl solution in EtOH. The polymer was filtered and dried in vacuum to constant weight.

## 3. Results and discussion

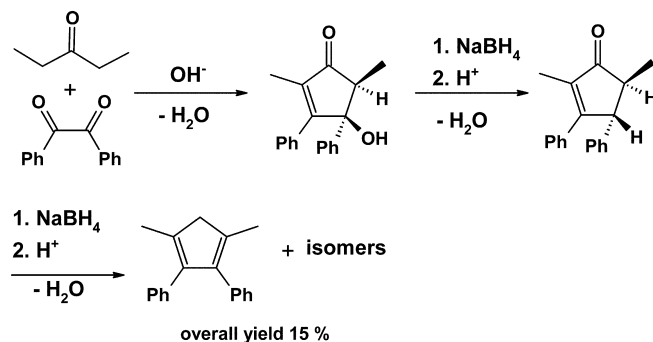
### 3.1. Preparation of 1,4-dimethyl-2,3-diphenylcyclopentadiene (**1**)

Compound **1** was prepared according to a reported synthetic procedure (Scheme 1) [8]. Although direct preparation of *trans*-2,5-dimethyl-3,4-diphenylcyclopent-2-en-1-one (as the key intermediate) by condensation of 3-pentanone with 2 equivalents of benzaldehyde catalyzed by ZrOCl<sub>2</sub>·8H<sub>2</sub>O was reported, the published conditions were compatible rather with a microscale preparation [15]. Recently it has been observed that replacement of ZrOCl<sub>2</sub>·8H<sub>2</sub>O catalyst by [TiCl<sub>4</sub>(THF)<sub>2</sub>] leads to higher yields and the reaction scale can be enlarged to a multigram quantity [16]. Nevertheless, the use of inert conditions still makes the reaction quite difficult. Thus, we preferred base-catalyzed condensation of 3-pentanone with benzil [17–19], followed by repeated reduction and acid-catalyzed dehydration providing **1** as a yellow crystalline solid (Scheme 1). In dependence on the conditions of the last dehydration step we obtained the desired product as cyclopentadiene with C<sub>2v</sub> symmetry or as a mixture of isomers. The cyclopentadiene **1** has very similar EI-MS pattern to previously prepared substitution isomer 2,3-dimethyl-1,4-diphenylcyclopentadiene (**I**) [7]. Both compounds have the molecular ion  $m/z$  246 as a base peak, whereas the abundance of other ions is rather low. On the other hand  $^1\text{H}$  NMR of C<sub>6</sub>D<sub>6</sub> solutions of the compounds are quite different showing remarkable redistribution of electron density as a consequence of different position of methyl and phenyl groups in **1** and **I**. As the most remarkable was a significant downfield shift of methylene protons in **1** compared to **I** (2.74 ppm in **1**, 3.47 ppm in **I**; for comparison: 1,2,3,4-tetramethylcyclopentadiene in CDCl<sub>3</sub> 2.60 ppm [20], 1,2,3,4-tetraphenylcyclopentadiene in C<sub>6</sub>D<sub>6</sub> 3.72 ppm [21]). The similar downfield shift was observed for all aromatic protons in **1** with respect to **I**. A lower stability

**Table 1**  
Crystallographic data, data collection and structure refinement data for compound **3**.<sup>a</sup>

Chemical formula	C <sub>38</sub> H <sub>34</sub> Cl <sub>2</sub> Zr
Molecular weight	652.77
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c (No. 14)
Temperature (K)	150(2)
<i>a</i> (Å)	21.7600(4)
<i>b</i> (Å)	14.9530(3)
<i>c</i> (Å)	19.2860(4)
$\alpha$ (°)	90.000
$\beta$ (°)	91.8930(13)
$\gamma$ (°)	90.000
<i>Z</i>	8
Crystal size (mm <sup>3</sup> )	0.50 × 0.05 × 0.05
<i>D</i> <sub>calc</sub> (g × cm <sup>-3</sup> )	1.383
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.546
<i>F</i> (000)	2688
$\theta$ range (°)	1.72–26.73
<i>hkl</i> range	–27/27, –15/18, –24/24
Reflections collected/unique	46774/13245
Parameters	747
<i>R</i> , <i>wR</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0403, 0.0727
<i>R</i> , <i>wR</i> (all data)	0.0761, 0.0842
<i>S</i>	1.011
$\Delta\rho_{\text{max,min}}$ (e Å <sup>-3</sup> )	0.362, –0.576

<sup>a</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR(F_2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ ,  $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffs}} - N_{\text{params}})]^{1/2}$ .

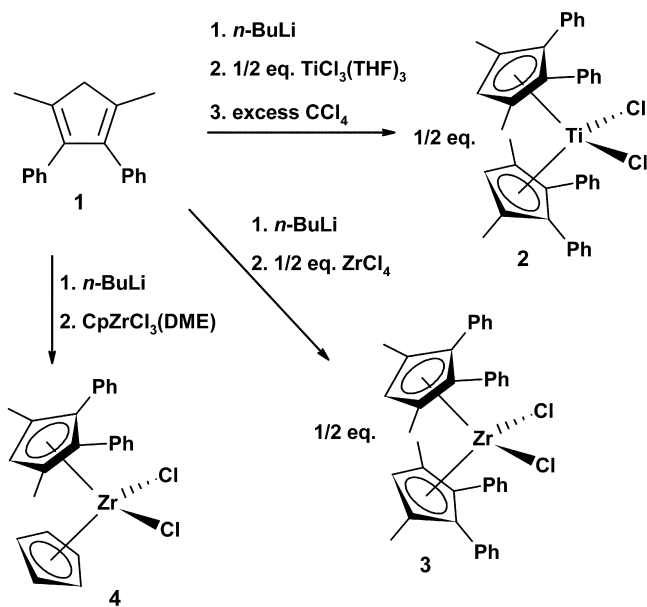


**Scheme 1.** Synthesis of 1,4-dimethyl-2,3-diphenylcyclopentadiene (**1**) as published in Ref. [8].

of **1** compared to **I** is to be noticed, since prolonged storage at room temperature led to the compound decomposition. We suggest that this behavior results from a lower extent of conjugation of cyclopentadiene and phenyl rings in **1**.

### 3.2. Preparation of group 4 metallocene dichlorides

Synthetic procedure for preparation of metallocene dichlorides **2–4** is depicted in Scheme 2. Deprotonation of ligand precursor **1** with *n*-butyllithium in diethyl ether affords lithium salt in almost quantitative yield. The reaction of two equivalents of the lithium salt with  $[\text{TiCl}_3(\text{THF})_3]$  in THF gives a titanocene chloride, whose oxidation with an excess of  $\text{CCl}_4$  yields titanocene dichloride **2** in moderate yield. The complex **2** crystallizes from toluene solution as hemisolvate with toluene as was detected by NMR spectroscopy and elementary analysis. The zirconocene dichloride **3** was prepared in modest yield by the reaction of  $\text{ZrCl}_4$  with two equivalents of the lithium salt of ligand **1** in boiling toluene.



Scheme 2. Preparation of complexes **2–4**.

For synthesis of complex **4** bearing different cyclopentadienyl ligands two synthetic pathways were attempted. Initially, a consecutive addition of the lithium salt of **1** and cyclopentadienyllithium to  $\text{ZrCl}_4$  was performed. The NMR characterization of crude product revealed a mixture of **4**, **3** and  $[\eta^5\text{-}(\text{C}_5\text{H}_5)_2\text{ZrCl}_2]$  in ratio 78:8:14. Although **3** was removed from the mixture by fractional crystallization, **4** could not be obtained in pure form due to its similar solubility to that of  $[\eta^5\text{-}(\text{C}_5\text{H}_5)_2\text{ZrCl}_2]$  (the final product still contained about 10% of  $[\eta^5\text{-}(\text{C}_5\text{H}_5)_2\text{ZrCl}_2]$ ). Therefore the reaction of lithium salt of **1** with  $[\eta^5\text{-}(\text{C}_5\text{H}_5)\text{ZrCl}_3(\text{DME})]$  was used as an alternative reaction pathway. The later reaction led to zirconocene dichloride **4** as a sole product in moderate yield.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2–4** showed the  $\text{C}_{2v}$  time averaged symmetry indicating free rotation of both cyclopentadienyl and phenyl rings at room temperature. All complexes displayed characteristic signals for methyl groups directly bonded to ring moiety with chemical shifts 2.06 ppm for **2**, 2.10 ppm for **3** and 2.01 ppm for **4**. The singlet signals belonging to the CH group of cyclopentadienyl ring appeared at 5.77 ppm for **2**, 5.69 ppm for **3** and 5.42 ppm for **4**.

EI-MS spectra of all complexes showed only low abundant molecular ions ( $m/z = 608$  for **2**,  $m/z = 652$  for **3** and  $m/z = 472$  for **4**), while the most abundant fragment ion was  $[\text{Cp}^*\text{MCl}_2]^+$ . All spectra showed a surprisingly abundant fragment  $m/z = 246$  which could be assigned to a protonated form of ligand  $[\text{Cp}^*\text{H}]^+$ , which is for **3** and **4** even more abundant than  $[\text{Cp}^*]^+$  ( $m/z = 245$ ).

### 3.3. Crystal structure analysis

The complex **3** crystallizes with two independent molecules (denoted **3a** and **3b**) in the unit cell (space group  $P2_1/c$ ). Molecular structures of molecules **3a** and **3b** are shown in Fig. 1, selected bond lengths and angles for both independent molecules are given in Table 2. The zirconium atoms have distorted tetrahedral environment with the Zr–Cl distances 2.4247(6) Å and 2.4262(7) Å for **3a** and 2.4103(8) Å and 2.4326(8) Å for **3b** which is close to other octasubstituted zirconocene dichlorides (average Zr–Cl distance in  $[\text{ZrCl}_2\{\eta^5\text{-}(\text{C}_5\text{Me}_4\text{H})\}_2]$  is 2.434(3) Å [22], in  $[\text{ZrCl}_2\{\eta^5\text{-}(\text{C}_5\text{H}\text{-}1,4\text{-Ph}_2\text{-}2,3\text{-Me}_2)\}_2]$  is 2.432(1) Å [7]). The dihedral angles between least-square planes of cyclopentadienyl rings are similar for both independent molecules ( $56.01(16)^\circ$  in **3a** and  $57.94(16)^\circ$  in **3b**). The values are comparable to the value found in  $[\text{ZrCl}_2\{\eta^5\text{-}(\text{C}_5\text{H}_2\text{-}1,2\text{-Ph}_2\text{-}4\text{-Me})\}_2]$  ( $56.8^\circ$ ) and substantially smaller than in corresponding nonmethylated analogue  $[\text{ZrCl}_2\{\eta^5\text{-}(\text{C}_5\text{H}_3\text{-}1,$

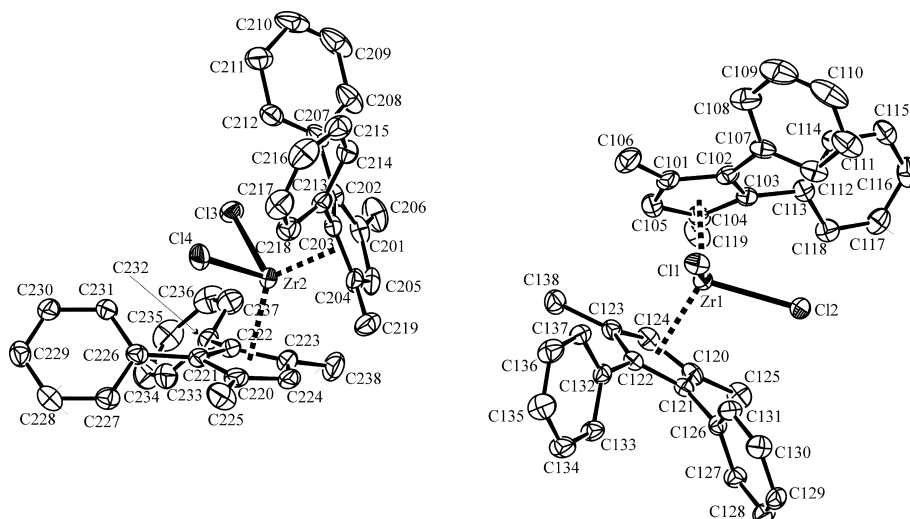


Fig. 1. Molecular structures of **3a** and **3b** (thermal ellipsoids are given with 30% probability). Hydrogen atoms are omitted for clarity.

**Table 2**  
Selected bond lengths (Å) and angles (°) for molecules **3a** and **3b**.<sup>a</sup>

<b>3a</b>			
Zr1–Cl1	2.4247(6)	Zr1–Cl2	2.4262(7)
Zr1–C <sub>g</sub> (1) <sup>b</sup>	2.2498(12)	Zr1–C <sub>g</sub> (2) <sup>b</sup>	2.2507(11)
Zr1–C <sub>ring</sub>	2.467(2)–2.624(2)		
C–C <sub>CP</sub> ring	1.404(4)–1.437(4)	C–C <sub>Ph</sub> ring	1.365(5)–1.400(4)
C <sub>ring</sub> –C <sub>Ph</sub>	1.479(4)–1.487(4)	C <sub>ring</sub> –C <sub>Me</sub>	1.503(4)–1.511(4)
Cl1–Zr1–Cl2	96.81(3)	C <sub>g</sub> (1)–Zr1–C <sub>g</sub> (2) <sup>b</sup>	130.21(4)
φ <sup>c</sup>	56.01(16)	τ <sup>d</sup>	56.35(4)
<b>3b</b>			
Zr2–Cl3	2.4326(8)	Zr2–Cl4	2.4103(8)
Zr2–C <sub>g</sub> (3) <sup>b</sup>	2.2432(13)	Zr2–C <sub>g</sub> (4) <sup>b</sup>	2.2495(12)
Zr2–C <sub>ring</sub>	2.468(3)–2.637(2)		
C–C <sub>CP</sub> ring	1.399(4)–1.433(4)	C–C <sub>Ph</sub> ring	1.363(6)–1.400(4)
C <sub>ring</sub> –C <sub>Ph</sub>	1.478(4)–1.485(4)	C <sub>ring</sub> –C <sub>Me</sub>	1.504(4)–1.508(4)
Cl3–Zr2–Cl4	94.60(3)	C <sub>g</sub> (3)–Zr2–C <sub>g</sub> (4) <sup>b</sup>	129.19(5)
φ <sup>c</sup>	57.94(16)	τ <sup>d</sup>	44.19(5)

<sup>a</sup>Extreme values in the two independent molecules **3a**, **3b** of the unit cell, the cyclopentadienyl ring atoms are denoted C101–C105 and C120–C124 for **3a**, and C201–C205 and C220–C224 for **3b** as shown in Fig. 1.

<sup>b</sup> C<sub>g</sub>(1), C<sub>g</sub>(2), C<sub>g</sub>(3) and C<sub>g</sub>(4) are centroids of the C(101–105), C(120–124), C(201–205) and C(220–224) cyclopentadienyl rings.

<sup>c</sup> Dihedral angle between the least-squares planes of the cyclopentadienyl rings.

<sup>d</sup> Torsion angles C(105)–C<sub>g</sub>(1)–C<sub>g</sub>(2)–C(124) and C(205)–C<sub>g</sub>(3)–C<sub>g</sub>(4)–C(224).

2-Ph<sub>2</sub>)<sub>2</sub>] (61.6°, 62.3°) [2]. Similarly the C<sub>g</sub>–Zr–C<sub>g</sub> angle value increases in the opposite order [ZrCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H<sub>3</sub>-1,2-Ph<sub>2</sub>)<sub>2</sub>}] (126.6° and 126.9°) [ZrCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H<sub>2</sub>-1,2-Ph<sub>2</sub>-4-Me)}] (129.5°) and **3** (130.21(4)° and 129.19(15)°). The both data reflect an increased crowding of open side of molecules with increasing number of methyl groups at the cyclopentadienyl rings. The cyclopentadienyl rings in **3a** and **3b** are staggered. Their mutual rotation, however, differs as indicated by torsion angles C(105)–C<sub>g</sub>(1)–C<sub>g</sub>(2)–C(124) 56.35° for **3a** and C(205)–C<sub>g</sub>(3)–C<sub>g</sub>(4)–C(224) 44.19° for **3b**. All phenyl groups are rotated away from coplanar conformation with cyclopentadienyl moiety, the dihedral angles between least-square planes of Cp' and Ph rings ranging 38.09(16)–55.16(14)°. This diminishes the conjugation of both aromatic systems.

### 3.4. Polymerization of ethylene

Complexes **2–4** (and [ZrCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}] for comparison) were activated by excess MAO and evaluated in polymerization of ethylene (Table 3). The complexes **3** and **4** showed only negligible activity at 30–50 °C, whereas at 80 °C they both possessed high activity at almost the same level (370–390 kg<sub>PE</sub>/mol<sub>Met</sub>/h). The dramatic increase of activity by raising temperature from 50 °C to 80 °C could be attributed to a steric crowding of the active center by the bulky phenyl and methyl groups. The crowding of the active site then influenced either formation of cationic centre by cocatalyst or insertion of ethylene into Zr–C bond. The influence of steric crowding on activation of bulky [Zr{Me<sub>2</sub>Si(η<sup>5</sup>-C<sub>5</sub>Ph<sub>4</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>t-Bu)}] by MAO was recently elucidated by DFT calculation, which showed

**Table 3**  
Comparison of **2–4**/MAO activity in ethylene polymerization.

Catalyst	T (°C)	t (h)	[M] × 10 <sup>4</sup> M	m <sub>PE</sub> (g)	Activity (kg <sub>PE</sub> /mol <sub>Met</sub> /h)	M <sub>v</sub> (kg mol <sup>-1</sup> )	T <sub>m</sub> (°C)
<b>2</b> /MAO	50	2	2.0	0.012	1		
<b>2</b> /MAO	80	2	2.0	0.028	1		
<b>3</b> /MAO	30	3	1.0	0.0002	0		
<b>3</b> /MAO	50	12	2.0	0.017	0		
<b>3</b> /MAO	80	1	1.0	1.939	388	10.6	130.7
<b>4</b> /MAO	50	2	2.0	0.032	2		
<b>4</b> /MAO	80	1	1.0	1.845	369	18.0	131.7
Cp <sub>2</sub> ZrCl <sub>2</sub> /MAO	30	1	1.0	0.721	144		
Cp <sub>2</sub> ZrCl <sub>2</sub> /MAO	80	1	1.0	3.748	750	11.4	129.0

Polymerization conditions: Al/M = 900 (M = Ti, Zr), toluene 50 ml, ethylene pressure 1.1 atm.

**Table 4**

The effect of catalyst/cocatalyst ratio on polymerization activity of zirconocene **3**/MAO system.

Al/Zr	[Zr] × 10 <sup>4</sup> M	m <sub>PE</sub> (g)	Activity (kg <sub>PE</sub> /mol <sub>Met</sub> /h)
200	2.4	0.103	4
500	1.8	1.089	61
900	1.6	3.526	221

Polymerization conditions: temperature 80 °C, polymerization time 2 h, toluene 50 ml, ethylene pressure 1.1 atm.

that the abstraction of a methyl group to form the cationic active species was endothermic (8.5 kcal/mol) [23]. Moreover, the DFT calculation showed that barrier for insertion of ethylene into Zr–Me bond is relatively high (12–24 kcal/mol for [Cp<sub>2</sub>ZrMe]<sup>+</sup>) [24,25]. Therefore, an elevated temperature is crucial for the polymerization promoted by catalysts derived from bulky **3** or **4**.

About half value of activity of complexes **3** and **4** in comparison with the standard [ZrCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}] at 80 °C can be attributed to a lower concentration of cationic active species during polymerization, because the electron-attracting phenyl substituents on cyclopentadienyl rings are known to destabilize the cationic center [26]. A low stability of cationic species is in line with the observed decrease in activity with lowering of the Al/Zr ratio at 80 °C (Table 4). However, it should be noted that is a general trend for most metallocene catalysts [27,28].

Molar masses of polyethylenes prepared using **3**, **4** and [ZrCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}] under given experimental conditions (Table 3) are in the range 10000–18000 g mol<sup>-1</sup>. These relatively low values are due to a low ethylene pressure, high reaction temperature (necessary for a reasonable propagation rate) and rather high catalyst concentration, all factors enabling β-H elimination and chain-transfer to aluminium as observed previously in [ZrCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}]/MAO catalyzed ethylene polymerization under similar conditions [29,30], the molar mass of polyethylene obtained with bulky complex **3**, for which the lower extent of β-H elimination could be expected, is surprisingly similar to molar mass of the polymer produced by the standard [ZrCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}] catalysts. In contrast, the highest molar mass polyethylene was obtained by less sterically hindered complex **4**. This shows the complexity of polymerization process in which the simultaneous propagation and chain-transfer reactions take place and their proportion determines final chain length. The melting transition temperatures of prepared polyethylene matrices (129.0–131.7 °C) are in range typical for linear polyethylene, about 10 °C lower than in the case of [ZrCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H<sub>3</sub>-1,2-Ph<sub>2</sub>)<sub>2</sub>}]/MAO catalyst [2]. This difference arise from different conditions for polymerization used in [2] (low temperature, high ethylene pressure, lower catalyst concentration) where chain-transfer reactions were significantly suppressed and polyethylenes with very high molar masses were prepared.

Contrary to catalysts derived from zirconocene dichlorides **3** and **4**, the catalyst formed from mixing **2** with MAO is practically inactive at any temperature. The same behavior was found in [TiCl<sub>2</sub>{η<sup>5</sup>-(C<sub>5</sub>H-1,4-Ph<sub>2</sub>-2,3-Me<sub>2</sub>)<sub>2</sub>}]/MAO system [7]. We suggested the behavior as a consequence of the reduction of a titanium cationic center to catalytically inactive Ti(III) center induced by MAO and/or trimethylaluminum (inherent part of MAO solutions). An easier reduction of titanocene dichlorides compared to zirconocene dichlorides is well known and was evaluated by cyclic voltammetry [31,32].

## 4. Conclusions

Combination of phenyl and methyl groups in the cyclopentadienyl ligand framework has a specific impact on catalysts performance. The catalysts formed from combination of MAO with

**3** or **4** required a high temperature and relatively high Al/Zr ratio to reach high ethylene polymerization activity. The determining factor is presumably the presence of electron-attracting bulky phenyl groups bonded to cyclopentadienyl moiety. A high tendency of titanium to reduction increased by the presence of electron-attracting phenyl groups is probably responsible for negligible activity of the catalyst derived from **2** at all studied temperatures.

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### Appendix A. Supplementary material

CCDC 679430 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.019.

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