

Titanium and zirconium complexes containing the new 2,3-dimethyl-1,4-diphenylcyclopentadienyl ligand. Synthesis, characterization and polymerization behavior

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Abstract

An easy and inexpensive three-step synthesis of new 2,3-dimethyl-1,4-diphenylcyclopentadiene (**3**) ligand and the titanium and zirconium homometallocene dichlorides [TiCl₂(η⁵-C₅H-2,3-Me₂-1,4-Ph₂)₂] (**4**), [ZrCl₂(η⁵-C₅H-2,3-Me₂-1,4-Ph₂)₂] (**5**), and the mixed ligand zirconium complex [ZrCl₂(η⁵-C₅H-2,3-Me₂-1,4-Ph₂)(η⁵-C₅H₅)] (**6**) prepared thereof are described. The polymerization of ethene using **4–6**/MAO catalysts revealed that zirconocene complexes **5** and **6** displayed moderate and high activity, respectively, whereas the titanium catalyst **4**/MAO was inactive. The crystal structures of **4** and **5** were determined by X-ray crystallography.

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1. Introduction

The discovery of methylalumoxane (MAO) in 1980 by Kaminsky and co-workers [1] led to a new application of Group 4 metallocenes as highly efficient catalysts for ethene polymerization. Simple zirconocene dichloride which showed the highest polymerization activity among early transition metallocene dichlorides [2] was soon modified by various substituents on the cyclopentadienyl rings strongly influencing the steric and electronic property of the catalytic center and its catalytic behavior, particularly in polymerization of propene and

olefin copolymerizations [3]. Particularly, the substitution of cyclopentadienyl rings in zirconocene dichlorides by phenyl group(s) modified the catalytic behavior of polymerization catalysts derived thereof for polymerization of ethene and other 1-alkenes [4–8]. The introduction of phenyl group in 2-position of indenyl rings in bis(indenyl)zirconium dichloride/MAO catalyst slowed down mutual rotation of the ligands to give transient racemic and meso rotamers, which consequently produced isotactic and atactic polypropylene blocs [9]. The highly phenylated cyclopentadienyl zirconocene dichloride [ZrCl₂{(η⁵-C₅Ph₅)(η⁵-C₅H₅)}] has been used for [4 + 2] cycloaddition of methyl- and ethylmethacrylate to cyclopentadiene [10].

In this paper, we report the synthesis of the new 2,3-dimethyl-1,4-diphenylcyclopentadienyl ligand, its titanocene and zirconocene complexes, and their catalytic activity in polymerization of ethene.

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2. Results and discussion

2.1. Synthesis of the ligand precursor

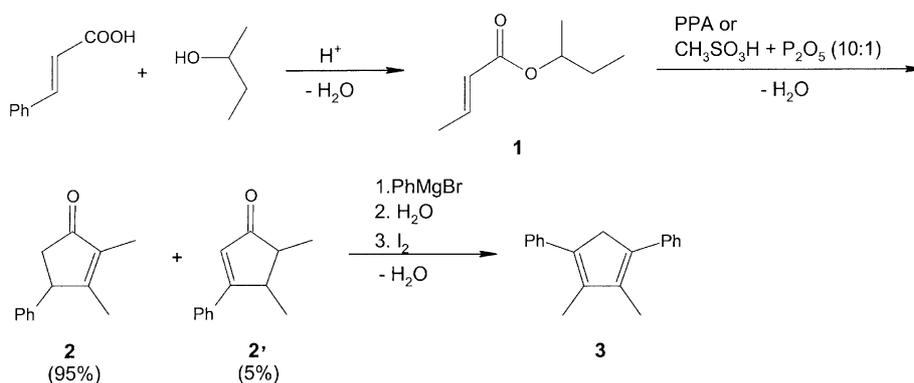
The synthesis of 2,3-dimethyl-1,4-diphenylcyclopenta-1,3-diene (**3**) (Scheme 1) was based on a modification of the method used for the preparation of tetramethylcyclopentenone [11]. 2-Butyl cinnamate (**1**) was prepared by acid-catalyzed esterification of cinnamic acid with 2-butanol in nearly quantitative yield [12]. The conversion of **1** to a mixture of cyclopentenones (**2** and **2'**) was accomplished both by polyphosphoric acid (PPA) [13] or by a solution of P_2O_5 in methanesulfonic acid [14]. The method using PPA is more convenient because it produces a purer product, and the **1**/PPA ratio (w/w) can be increased to 1:5 against the reported ratio 1:8 [13] or 1:45 [15] without any significant change in yield. Moreover, the hydrolysis of PPA at elevated temperature (40–50 °C) facilitates the product isolation. In both cases, 1H NMR and ^{13}C NMR analysis indicated that a mixture of 2,3-dimethyl-4-phenylcyclopent-2-enone (**2**) (ca. 95%) and 4,5-dimethyl-3-phenylcyclopent-2-enone (**2'**) (ca. 5%) was obtained. The mixture of cyclopentenones (**2** + **2'**) was reacted with an excess of phenylmagnesium bromide, the product was hydrolyzed to give the corresponding alcohol, and its iodine-catalyzed dehydration produced 2,3-dimethyl-1,4-diphenylcyclopentadiene (**3**) as the only isomer in overall yield of 25%. The 1H NMR spectrum of **3** showed a down-field shift of the signal for methylene protons (δ 3.47 ppm) compared to that in

tetramethylcyclopentadiene (δ 2.60 ppm) [16], apparently resulting from an electron-withdrawing effect of the two phenyl groups.

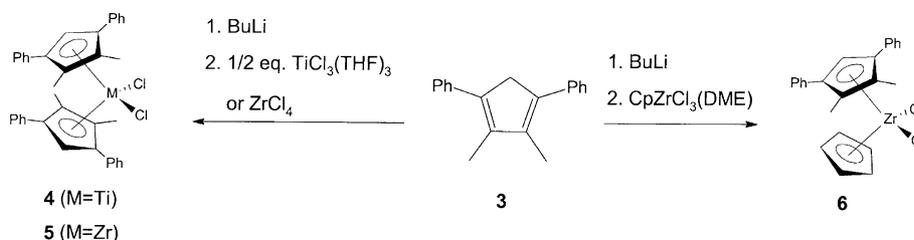
2.2. Synthesis of metallocene dichlorides **4**, **5**, and **6**

Syntheses of the metallocene dichlorides were carried out using standard methods (Scheme 2). Corresponding anions were obtained by conventional reaction of 2,3-dimethyl-1,4-diphenylcyclopenta-1,3-diene (**3**) with one equivalent of *n*-butyllithium in diethyl ether at 0 °C. A treatment of the ligand anion with 0.5 equivalent of $TiCl_3(THF)_3$ in tetrahydrofuran (THF) gave, after oxidation by CCl_4 and recrystallization from a toluene/hexane mixture bis(η^5 -2,3-dimethyl-1,4-diphenylcyclopentadienyl)dichlorotitanium (**4**) as deep red crystals in 76% yield. Similarly, the reaction of two equivalents of the above lithium salt with $ZrCl_4$ in toluene gave yellow crystalline bis(η^5 -2,3-dimethyl-1,4-diphenylcyclopentadienyl)dichlorozirconium (**5**) in yield of 62%. The zirconium complex with mixed ligands (η^5 -2,3-dimethyl-1,4-diphenylcyclopentadienyl)(η^5 -cyclopentadienyl)dichlorozirconium (**6**) was prepared by reacting lithium salt of **3** with $[CpZrCl_3(DME)]$. All the complexes **4–6** in the solid state were air and moisture stable.

The identity of compounds was deduced from their 1H and ^{13}C NMR spectra, IR and EI-MS spectra, and elemental analyses. Crystal structures of **4** and **5** were determined by X-ray diffraction analysis (see below). The NMR and IR spectra mainly proved the presence of η^5 -bonded ligand anions of **3**, and NMR spectra did not



Scheme 1.



Scheme 2.

indicate signs of restricted rotation of the cyclopentadienyl ligands and phenyl substituents at room temperature. The mass spectra proved the expected molecular compositions and revealed considerable differences in fragmentation patterns of the complexes. While in the mass spectrum of **5** the $[M-C_5Me_2Ph_2H]^+$ ion was the base peak, in the spectrum of **4** the $[M-C_5Me_2Ph_2H]^+$ fragment had a relative abundance of only (16%) and $[C_5Me_2Ph_2H]^+$ was the base peak. This fragmentation behavior reflects a higher electropositivity of zirconium compared to titanium and a larger steric congestion in **4** compared to **5**. In EI-MS spectrum of **6** the $[M-C_5H_5]^+$ ion was more abundant than the $[M-CpMe_2Ph_2H]^+$ ion.

2.3. Crystal structure of **4** and **5**

The structures of **4** and **5** were determined by single crystal X-ray diffraction analysis. The selected bond lengths and angles are given in Table 1. The isomor-

phous complexes crystallize in the monoclinic $P2_1/c$ space group with two crystallographically independent molecules (denoted **4a** and **4b** for compound **4**, and **5a** (Fig. 1) and **5b** for compound **5**) in the unit cell, which differentiate mainly in orientations of phenyl groups. Compounds **4** and **5** differ mainly in the lengths of M–Cg (Cg-centroid of the cyclopentadienyl ring) and M–Cl bonds, the difference being caused mainly by different covalent radii of both the metals. This difference has, however, no effect on dihedral angles between least-squares planes of cyclopentadienyl rings (ϕ) which amount to $54.61(10)^\circ$ and $55.57(12)^\circ$ for **4**, and $54.34(6)^\circ$ and $56.10(7)^\circ$ for **5**. The Cg–M–Cg angles for **4a** ($133.70(5)^\circ$), **4b** ($130.00(5)^\circ$), **5a** ($132.11(3)^\circ$), and **5b** ($130.84(3)^\circ$) are in the range typical for octamethyl-substituted titanocene- and zirconocene dichlorides (see Table 2). The less substituted metallocene dichlorides show smaller angles due to a relieve of steric hindrance between the cyclopentadienyl ligands: 130.8° in

Table 1
Selected bond lengths (Å) and angles ($^\circ$) for non-equivalent molecules of **4** and **5**^a

4a			
Ti1–Cl1	2.331(1)	Ti1–Cl2	2.332(1)
Ti1–Cg(1) ^b	2.139(1)	Ti1–Cg(2) ^b	2.128(1)
Ti1–C _{ring}	2.351(3)–2.548(3)		
C–C _{Cp ring}	1.395(4)–1.434(4)	C–C _{Ph ring}	1.345(6)–1.404(4)
C _{ring} –C _{Ph}	1.475(4)–1.483(4)	C _{ring} –C _{Me}	1.489(4)–1.500(4)
Cl1–Ti1–Cl2	93.63(3)	Cg(1)–Ti1–Cg(2) ^b	133.70(5)
ϕ^c	54.61(10)	τ^d	37.5(2)
4b			
Ti2–Cl4	2.327(1)	Ti2–Cl3	2.343(1)
Ti2–Cg(3) ^b	2.136(1)	Ti2–Cg(4) ^b	2.132(1)
Ti2–C _{ring}	2.365(3)–2.533(3)		
C–C _{Cp ring}	1.401(4)–1.429(4)	C–C _{Ph ring}	1.353(6)–1.401(4)
C _{ring} –C _{Ph}	1.480(4)–1.485(4)	C _{ring} –C _{Me}	1.494(4)–1.507(4)
Cl3–Ti2–Cl4	91.40(4)	Cg(3)–Ti2–Cg(4) ^b	130.00(5)
ϕ^c	55.57(12)	τ^d	40.5(2)
5a			
Zr1–Cl1	2.423(1)	Zr1–Cl2	2.432(1)
Zr1–Cg(1) ^b	2.243(1)	Zr1–Cg(2) ^b	2.240(1)
Zr1–C _{ring}	2.461(2)–2.630(2)		
C–C _{Cp ring}	1.413(2)–1.437(2)	C–C _{Ph ring}	1.374(3)–1.406(2)
C _{ring} –C _{Ph}	1.475(2)–1.486(2)	C _{ring} –C _{Me}	1.497(2)–1.505(2)
Cl1–Zr1–Cl2	93.83(2)	Cg(1)–Zr1–Cg(2) ^b	132.11(3)
ϕ^c	54.34(6)	τ^d	36.37(4)
5b			
Zr2–Cl4	2.429(1)	Zr2–Cl3	2.443(1)
Zr2–Cg(3) ^b	2.247(1)	Zr2–Cg(4) ^b	2.245(1)
Zr2–C _{ring}	2.480(2)–2.620(2)		
C–C _{Cp ring}	1.412(2)–1.433(2)	C–C _{Ph ring}	1.384(3)–1.403(3)
C _{ring} –C _{Ph}	1.479(3)–1.489(2)	C _{ring} –C _{Me}	1.494(3)–1.505(2)
Cl3–Zr2–Cl4	92.21(2)	Cg(3)–Zr2–Cg(4) ^b	130.84(3)
ϕ^c	56.10(7)	τ^d	37.81(4)

^a Extreme values in the two independent molecules of the unit cell, the cyclopentadienyl ring atoms are denoted C101–C105 as shown in Fig. 1.

^b Cg(1), Cg(2), Cg(3) and Cg(4) are centroids of the C(101–105), C(120–124), C(201–205), and C(220–224) cyclopentadienyl rings.

^c Dihedral angle between the least-squares planes of the cyclopentadienyl rings.

^d Torsion angles C(105)–Cg(1)–Cg(2)–C(124) and C(205)–Cg(3)–Cg(4)–C(224).

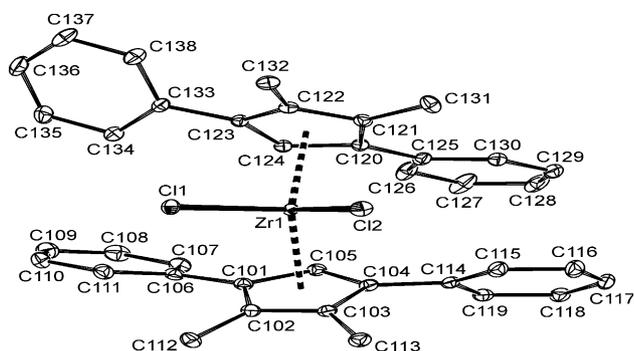


Fig. 1. Molecular structure of **5a** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. The hydrogen atoms are omitted for clarity.

$[\text{ZrCl}_2\{\eta^5\text{-}(\text{C}_5\text{H}_2\text{-}1,3\text{-Ph}_2\text{-}2\text{-}(\text{C}_4\text{H}_9))_2\}][6]$, 126.6° in $[\text{ZrCl}_2\{\eta^5\text{-}(\text{C}_5\text{H}_3\text{-}1,2\text{-Ph}_2)_2\}][8]$, and 126.9° in $[\text{C}_5\text{H}_4(\text{C}_6\text{F}_5)_2\text{TiCl}_2][20]$. The phenyl groups are substantially rotated away from conjugative coplanar orientation showing the following dihedral angles between the least-squares planes of phenyl and cyclopentadienyl rings: $22.41(11)^\circ$, $43.55(11)^\circ$, $12.70(19)^\circ$, $36.23(16)^\circ$ for **4a**; $40.57(14)^\circ$, $35.28(15)^\circ$, $43.16(13)^\circ$, $38.88(13)^\circ$ for **4b**; $22.14(6)^\circ$, $43.08(6)^\circ$, $11.58(11)^\circ$, $36.42(9)^\circ$ for **5a** and $40.93(8)^\circ$, $33.94(9)^\circ$, $43.40(7)^\circ$, $39.45(7)^\circ$ for **5b**. Both complexes have almost ideal staggered conformation with the unsubstituted carbon atoms placed at hinge positions, torsion angles $\text{C}(\text{H})\text{-Cg-Cg-C}(\text{H})$ being $37.5(2)^\circ$ for **4a**, $40.5(2)^\circ$ for **4b**, $36.37(4)^\circ$ for **5a**; $37.81(4)^\circ$ for **5b**. On the other hand, the values for Cl-M-Cl angles in **4** ($93.63(3)^\circ$ in **4a** and $91.40(4)^\circ$ in **4b**) and **5** ($93.83(2)^\circ$ in **5a** and $92.21(2)^\circ$ in **5b**) are considerably smaller (especially in **5**) than in octamethylated metallocene dichlorides (Table 2), which can be related to an electron-withdrawing effect of phenyl groups.

2.4. Ethene polymerization

The zirconium catalyst MAO/**5** showed a moderate activity while the analogous MAO/**6** catalyst was by one

Table 3
Polymerization of ethene with **5**, **6** and $\text{Cp}_2\text{ZrCl}_2^a$

No.	Catalyst	Yield PE (g)	A^b ($\times 10^{-3}$)	T_m^c ($^\circ\text{C}$)
1.	5	0.106	0.42	138.8
2.	5	0.099	0.40	
3.	6	1.02	4.1	137.8
4.	6	1.08	4.3	
5.	Cp_2ZrCl_2	1.02	4.1	138.1
6.	Cp_2ZrCl_2	0.90	3.6	

^a Polymerization conditions: $[\text{Zr}] = 2.5 \times 10^{-6} \text{ mol l}^{-1}$, MAO used as co-catalyst (Al:Zr = 10,000:1), 50 ml of toluene, temperature 20°C , ethylene pressure 4 bar, time 30 min.

^b $[A]$ (activity) = kg PE / [(mol Zr) h bar].

^c Melting temperature of PE determined by DSC.

order more productive (see Table 3). Both the catalysts gave high molecular weight polyethene of HDPE type as evidenced by melting points spanned over a narrow range of $137.8\text{--}138.8^\circ\text{C}$. A much higher activity of the MAO/**6** catalyst is apparently caused by a lower steric congestion at the zirconium cationic polymerization center. The contribution of the net electronic effect resulting from replacement of bulky 2,3-dimethyl-1,4-diphenylcyclopentadienyl ligand by unsubstituted cyclopentadienyl is difficult to estimate as the geometry of the metallocene skeleton seems to influence the energy gap between the HOMO and LUMO orbitals [21]. On the other hand, the MAO/**4** catalytic system was practically inactive for polymerization of ethene. The absence of polymerization activity is apparently related to an immediate colour change to blue upon addition of MAO to the red toluene solution of **4** saturated with ethene. It indicates an easy reduction of Ti(IV) to Ti(III) which is facilitated in **4** by an electron-withdrawing effect of four phenyl groups decreasing the electron density on the titanium atom. This is in accord with a poor polymerization activity of another strong but sterically less demanding Lewis acid: $[\text{C}_5\text{H}_4(\text{C}_6\text{F}_5)_2\text{TiCl}_2][20]$. A poor ethene polymerization activity of titanocene catalysts which underwent the reduction to Ti(III) is well known [22].

Table 2
Selected bond distances and angles for octa-substituted titanocene and zirconocene dichlorides

	M-Cg ^{a,b} (Å)	M-Cl ^b (Å)	Cg-M-Cg ^a ($^\circ$)	$\angle(\text{Cp-Cp})^c$ ($^\circ$)	Cl-M-Cl ($^\circ$)	Torsion angle ($^\circ$)	Ref.	
4	2.136(1)	2.332(1)	133.70(5)	54.61(10)	93.63(3)	37.5(2)	This work	
	2.134(1)	2.335(1)	130.00(5)	55.57(12)	91.40(4)	40.5(2)		
	$[\text{TiCl}_2(\eta^5\text{-C}_5\text{HMe}_4)_2]$	2.109	2.344(2)	133.4	54.4	94.2(1)	36.0	[17]
	$[\text{TiCl}_2(\eta^5\text{-C}_5\text{HPh}_4)_2]$	2.157(8)	2.317(1)	132.7(3)	59.69	96.8(1)	37.66	[18]
		2.161(3)	2.300(2)	133.6(7)	59.63	97.1(1)	40.78	
5	2.242(1)	2.428(1)	132.11(3)	54.34(6)	93.83(2)	36.37(4)	This work	
	2.246(1)	2.436(1)	130.84(3)	56.10(7)	92.21(2)	37.81(4)		
	$[\text{ZrCl}_2(\eta^5\text{-C}_5\text{HMe}_4)_2]$	2.226(3)	2.434(3)	133.1(1)	53.7(4)	97.61(9)	–	[19]

^a Cg means ring centroid of the five-membered cyclopentadienyl ring.

^b Average distance and standard deviation.

^c Dihedral angle between the least-squares planes of the cyclopentadienyl rings.

3. Experimental

3.1. General procedures

All reactions with moisture- and air-sensitive compounds were carried out under argon atmosphere using standard Schlenk techniques. Solvents diethyl ether, tetrahydrofuran (THF), hexane, and toluene were dried by potassium benzophenone or Na–K alloy, and freshly distilled prior to use. Cinnamic acid, 2-butanol, polyphosphoric acid (PPA), phenyl bromide, $ZrCl_4$ and butyllithium (1.6 M in hexane) were obtained from Aldrich and used as received. $TiCl_3(THF)_3$ [23] and $CpZrCl_3(DME)$ [24] were prepared according to literature procedures. 1H NMR (500 MHz) and ^{13}C NMR (125 MHz) were measured on a Bruker DRX500 spectrometer in C_6D_6 or $CDCl_3$ solution at 300 K. Chemical shifts are given relative to the solvent signal (δ_H 7.15, δ_C 128.00 for C_6D_6 and δ_H 7.26, δ_C 77.36 for $CDCl_3$). Mass spectra were measured on a KRATOS Concept 32S instrument (Centre de Spectroscopie Moléculaire de l'Université de Bourgogne). Infrared spectra were recorded on a Nicolet Avatar FT-IR spectrometer in the range 400–4000 cm^{-1} . Elemental analyses were performed on a FISON EA 1108 CHNS instrument by the Service de microanalyses du L.S.E.O. (Université de Bourgogne). Melting points were measured on Koffler block and were uncorrected. Melting points of polyethylenes were determined by DSC (Mettler 182E differential scanning calorimeter) at a heating range of 10 $^{\circ}C\ min^{-1}$.

3.2. Preparation of 2-butylester of cinnamic acid (1)

Cinnamic acid (50 g, 0.34 mol) and a 3-fold molar excess of 2-butanol (100 ml) were mixed with toluene (200 ml), and concentrated sulphuric acid (2 ml) was added. The mixture was refluxed under Dean-Stark adapter until water was separating (for 20 h). A slightly yellow mixture was subsequently washed with saturated water solution of Na_2CO_3 , water, and dried over Na_2SO_4 . The solution was concentrated in a rotary evaporator and a residue was fractionally distilled in vacuum. The core fraction distilled at 94–96 $^{\circ}C/0.5$ mmHg (lit. 122 $^{\circ}C/2$ mmHg [12]) as a colourless liquid. Yield 67.4 g (97%).

1H NMR (C_6D_6): 0.79 (t, $^3J_{HH} = 7.5$ Hz, 3H, $CH_3CHCH_2CH_3$), 1.12 (d, $^3J_{HH} = 6.5$ Hz, 3H, $CH_3CHCH_2CH_3$), 1.34–1.43 (m, 1H, $CH_3CHCH_2CH_3$), 1.49–1.58 (m, 1H, $CH_3CHCH_2CH_3$), 5.00 (pseudosextet, 1H, $CH_3CHCH_2CH_3$), 6.41 (d, $^3J_{HH} = 16.0$ Hz, 1H, $CH=CHPh$), 6.98–7.06 (m, 3H, Ph), 7.16–7.20 (m, 2H, Ph), 7.74 (d, $^3J_{HH} = 16.0$ Hz, 1H, $CH=CHPh$). $^{13}C\{^1H\}$ (C_6D_6): 9.81 ($CH_3CHCH_2CH_3$), 19.61 ($CH_3CHCH_2CH_3$), 29.19 ($CH_3CHCH_2CH_3$), 71.98 ($CH_3CHCH_2CH_3$), 119.34 ($CH=CHPh$), 128.21, 128.93, 130.07 (CH,

Ph), 134.94 (C_q , Ph), 144.26 ($CH=CHPh$), 166.09 (CO). EI-MS, m/z (relative abundance): 205 (11), 204 (M^+ ; 46), 175 (8), 159 (7), 149 (69), 148 ($[M-CH_3CHCH_2-CH_3]^+$; 88), 147 (85), 146 (19), 132 (52), 131 ($[M-CH_3CH(O)CH_2CH_3]^+$; 100), 120 (13), 104 (55), 103 ($[PhCH=CH]^+$; 83), 102 (51), 91 (15), 77 ($[Ph]^+$; 78), 74 (49), 73 (23). IR (neat, cm^{-1}): 3062 (vw), 3029 (vw), 2974 (m), 2937 (w), 2879 (w), 1709 (vs), 1638 (s), 1578 (w), 1496 (w), 1450 (m), 1379 (w), 1355 (m), 1311 (s), 1273 (s), 1203 (s), 1175 (vs), 1126 (m), 1115 (m), 1095 (m), 1072 (w), 1028 (m), 980 (m), 891 (w), 865 (w), 838 (vw), 768 (s), 733 (vw), 711 (m), 685 (m), 590 (vw), 572 (w), 542 (vw), 486 (w).

3.3. Preparation of 2,3-dimethyl-4-phenylcyclopent-2-enone (2)

3.3.1. Method A

PPA (500 g) was heated to 120 $^{\circ}C$ under mechanical stirring and 2-butyl cinnamate (71 g) was added in one portion. Then, the heating was stopped, a deep red mixture was stirred for 30 min, and was quenched by careful pouring on 500 ml of vigorously stirred slurry of ice in water. A resulting dark red–brown emulsion was stirred for another 30 min at 40 $^{\circ}C$ and then a red oil separated from water phase. The water phase was extracted twice with 200 ml of diethyl ether. The organic phases were combined, washed subsequently with saturated water solution of Na_2CO_3 and 50 ml of saturated $NaCl$ solution, and dried over Na_2SO_4 . The solvent was evaporated and the residue was distilled under vacuum. The fraction collected at 111–113 $^{\circ}C/1$ mmHg partly solidified at room temperature. Yield 27.4 g (42%). As revealed from NMR measurements the product consisted of two isomers: 2,3-dimethyl-4-phenylcyclopent-2-enone (2) (95%) and 3-phenyl-4,5-dimethylcyclopent-2-enone (2') (5%). The isomer 2 was isolated as white crystals from ether/pentane solution.

2: m.p. 57–58 $^{\circ}C$. 1H NMR (C_6D_6): 1.35 (s, 3H, CH_3 [β CO]); 1.66 (q, $^5J_{HH} = 1.0$ Hz, 3H, CH_3 , [α CO]); 2.16 (dd, $^2J_{HH} = 18.0$ Hz, $^3J_{HH} = 2.5$ Hz, 1H, H [β CO]); 2.57 (dd, $^2J_{HH} = 18.0$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, H [β CO]); 3.22–3.26 (m, 1H, H [β CO]); 6.75–6.80 (m, 2H, Ph); 7.00–7.09 (m, 3H, Ph). $^{13}C\{^1H\}$ (C_6D_6): 8.23 (CH_3 [α CO]); 14.92 (CH_3 [β CO]); 44.51 (CH_2); 49.02 ($CHPh$); 127.01, 128.52, 129.03 (CH, Ph); 136.99, 142.76, 169.47 ($[CO]$, [α CO] and Ph); 206.67 (CO). EI-MS, m/z (relative abundance): 187 (27), 186 (M^+ ; 82), 171 ($[M-Me]^+$; 68), 158 ($[M-CO]^+$; 45), 144 (26), 143 ($[M-MeCO]^+$; 100), 142 (25), 141 (37), 129 (42), 128 ($[M-MeCO-Me]^+$; 79), 127 (24), 115 (66), 109 (13), 104 (52), 103 (49), 102 (23), 91 (33), 78 (54), 77 ($[Ph]^+$; 65), 65 (24), 63 (20). IR (KBr, cm^{-1}): 3368 (w), 3053 (w), 2917 (m), 1689 (vs), 1643 (vs), 1600 (m), 1497 (m), 1455 (m), 1409 (m), 1378 (m), 1322 (s), 1281 (w), 1233 (vw), 1198

(vw), 1176 (w), 1142 (vw), 1070 (m), 932 (m), 918 (w), 879 (vw), 784 (w), 766 (s), 722 (w), 705 (s), 658 (w), 640 (vw), 581 (vw), 541 (vw), 486 (m), 468 (vw).

2': ^1H NMR (C_6D_6): 0.86 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, CH_3 [βCO]), 1.13 (d, $^3J_{\text{HH}} = 7.5$ Hz, 3H, CH_3 [αCO]), 1.87–1.93 (m, 1H, H [αCO]), 2.57–2.63 (partially overlapped by major isomer signal, m, 1H, H [βCO]), 6.26 (d, $^4J_{\text{HH}} = 1.0$ Hz, 1H, $=\text{CH}$), Ph signals are overlapped by signals of major isomer. ^{13}C $\{^1\text{H}\}$ (C_6D_6): 15.96 (CH_3 [αCO]), 19.36 (CH_3 [βCO]), 43.80 (CH [βCO]), 50.13 (CH [αCO]), 123.65 (olefinic C), 127.29, 128.89, 130.35 (CH , Ph), 134.18, 176.00 (C_q ; Ph and [βCO]), 208.57 (CO).

3.3.2. Method B

2-Butyl cinnamate (21 g, 0.1 mol) was added to 190 g of a 1:10 mixture $\text{P}_2\text{O}_5\text{--CH}_3\text{SO}_3\text{H}$ and the mixture was stirred for 2 h at room temperature. Resulting deep red oil was transferred to separatory funnel and slowly dropped to 300 ml of vigorously stirred water. The product was extracted with chloroform (4×100 ml). Combined organic phases were washed subsequently with saturated water solution of Na_2CO_3 and 50 ml of saturated NaCl solution, and dried over Na_2SO_4 . The solvent was evaporated and the residue was distilled at low pressure. A slightly yellow liquid was obtained at 100–102 °C/0.5 mmHg. Yield 8.2 g (43%). According to NMR analysis the product contained in addition to isomers **2** and **2'** ca. 10% of starting 2-butyl cinnamate.

3.4. Preparation of 2,3-dimethyl-1,4-diphenylcyclopenta-1,3-diene (**3**)

A solution of phenylbromide (12.2 g, 78 mmol) in 40 ml of diethyl ether was added dropwise to magnesium turnings (2.3 g, 95 mmol) in diethyl ether (150 ml) at the rate maintaining a mild reflux. After the reaction ceased, the mixture was refluxed for 30 min. After cooling, a mixture of dimethylphenylcyclopentenones (14.1 g, 76 mmol) in 50 ml of diethyl ether was slowly added, and the reaction mixture was refluxed for 2 h. Resulting grey–green mixture was poured onto a 100 ml mixture of ice and water acidified with 10 ml of concentrated HCl . The product was extracted with diethyl ether (4×100 ml), volume of combined organic phases was reduced to ca. 100 ml, and a few crystals of iodine were added. After standing overnight solid **3** was obtained as a result of the alcohol dehydration. The crude product was washed with large amount of ethanol and dried in vacuum to give 11.5 g (62%) of white crystalline solid.

m.p. 156–157 °C. ^1H NMR (C_6D_6): 1.94 (t, $^5J_{\text{HH}} = 1.8$ Hz, 6H, $=\text{CCH}_3$), 3.47 (septuplet, $^5J_{\text{HH}} = 1.8$ Hz, 2H, CH_2), 7.10 (tt, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, 2H,

Ph), 7.21–7.28 (m, 4H, Ph), 7.30–7.35 (m, 4H, Ph). ^{13}C $\{^1\text{H}\}$ (C_6D_6): 13.00 (CH_3), 45.51 (CH_2), 126.20, 128.14, 128.61 (CH , Ph), 138.16, 138.77, 139.84 (C_q ; C--CH_3 , C--Ph and Ph). EI-MS, m/z (relative abundance): 247 (23), 246 (M^+ ; 100), 231 ($[\text{M--Me}]^+$; 15), 216 (12), 215 (18), 149 (18), 148 (10), 131 (18), 115 (10), 103 (11), 77 ($[\text{Ph}]^+$; 12). IR (KBr, cm^{-1}): 3048 (s), 2991 (s), 2939 (s), 2917 (s), 2887 (s), 1957 (w), 1621 (w), 1595 (m), 1574 (w), 1492 (s), 1449 (s), 1437 (s), 1394 (w), 1371 (m), 1313 (w), 1279 (vw), 1202 (m), 1182 (w), 1158 (vw), 1106 (w), 1066 (m), 1026 (w), 1001 (w), 982 (w), 924 (w), 884 (vw), 756 (vs), 731 (vw), 707 (vs), 654 (vw), 600 (vw), 575 (vw), 542 (w), 472 (vw). Calc. for $\text{C}_{19}\text{H}_{18}$: C, 92.64; H, 7.36. Found: C, 92.41; H, 7.51%.

3.5. Preparation of bis(η^5 -2,3-dimethyl-1,4-diphenylcyclopentadienyl)dichlorotitanium (**4**)

Hexane solution of butyllithium (5.40 ml, 1.6 M, 8.6 mmol) was dropwise added to a pre-cooled solution of **3** (1.924 g, 7.82 mmol) in 60 ml of diethyl ether. The reaction mixture was warmed to room temperature and stirred overnight. A white precipitate was filtered, washed with diethyl ether (3×10 ml), and dissolved in 40 ml of THF. This solution was cooled to -78 °C and $\text{TiCl}_3(\text{THF})_3$ (1.449 g, 3.91 mmol) was successively added. The reaction mixture was slowly warmed to room temperature and then refluxed for 12 h. The resulting dark green mixture was cooled to room temperature and carbon tetrachloride (2 ml) was added, immediately turning the colour to deep red. After 1 h stirring at 40 °C, the solvents were evaporated under vacuum, and a solid residue was extracted with toluene (5×20 ml). The volume of dark red toluene extracts was concentrated to ca. 10 ml and the solution was layered with pentane (30 ml). Dark red crystals which grew up after several hours were isolated. Yield 1.80 g (76%).

m.p. 276 °C. ^1H NMR (C_6D_6): 2.28 (s, 6H, $\text{Cp}(\text{CH}_3)_2$), 6.55 (s, 1H, CpH), 6.88–6.93 (m, 4H, Ph), 6.97 (tt, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, 2H, $\text{C}(4)\text{H}$, Ph), 7.11–7.14 (m, 4H, Ph). ^{13}C $\{^1\text{H}\}$ (C_6D_6): 14.34 (CpCH_3), 111.30 (CH , $\text{CpMe}_2\text{Ph}_2\text{H}$), 127.35, 128.24, 128.91 (CH , Ph), 130.55, 134.40, 136.15 (C_q ; C--CH_3 , C--Ph and Ph). EI-MS, m/z (relative abundance): 610 (5), 609 (4), 608 (M^+ ; 8), 573 ($[\text{M--Cl}]^+$; 9), 365 (11), 364 (5), 363 ($[\text{M--C}_5\text{Me}_2\text{Ph}_2\text{H}]^+$; 16), 347 (8), 246 (29), 245 ($[\text{C}_5\text{Me}_2\text{Ph}_2\text{H}]^+$; 100), 244 (8), 230 (14), 229 (16), 228 (13), 215 (18), 167 (7), 165 (10), 115 (8). IR (KBr, cm^{-1}): 3052 (m), 3030 (w), 2917 (s,b), 2855 (s,b), 1598 (m), 1575 (w), 1518 (vw), 1493 (w), 1473 (w), 1448 (m), 1374 (w), 1202 (vw), 1182 (vw), 1154 (vw), 1107 (w), 1067 (w), 1028 (w), 1002 (vw), 981 (vw), 917 (vw), 788 (vs,b), 763 (s), 697 (s), 674 (m), 659 (m), 646 (m), 611 (w), 585 (w), 542 (vw), 500 (vw), 415 (m). Calc. for $\text{C}_{38}\text{H}_{34}\text{Cl}_2\text{Ti}$: C, 74.89; H, 5.62. Found: C, 75.23; H, 6.14%.

3.6. Preparation of bis(η^5 -2,3-dimethyl-1,4-diphenylcyclopentadienyl)dichlorozirconium (**5**)

Zirconium tetrachloride (0.655 g, 2.81 mmol) was added to a mixture of 2,3-dimethyl-1,4-diphenylcyclopentadienyl lithium salt (1.417 g, 5.62 mmol, prepared as for **4**) in 50 ml of toluene and the mixture was refluxed for 2 days. Then, the resulting mixture was filtered, a clear brown filtrate was reduced in volume to ca. 7 ml and cooled to $-18\text{ }^\circ\text{C}$ to afford a yellow powder of **5**. The product was isolated, washed with pentane (2×5 ml) and dried in vacuum. Yield 1.14 g (62%).

m.p. $231\text{ }^\circ\text{C}$. ^1H NMR (C_6D_6): 2.20 (s, 6H, Cp(CH₃)₂), 6.28 (s, 1H, CpH), 6.92–7.00 (m, 6H, Ph), 7.16–7.19 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): 13.37 (CpCH₃), 107.60 (CH, CpMe₂Ph₂H), 127.05, 128.47, 128.71 (CH, Ph), 130.36, 134.06 (C_q; C–Ph and Ph). ^1H NMR (CDCl_3): 2.28 (s, 6H, Cp(CH₃)₂), 6.29 (s, 1H, CpH), 7.03–7.10 (m, 6H, Ph), 7.14 (tt, $^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, 2H, C(4)H, Ph). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): 13.68 (CpCH₃), 107.81 (CH, CpMe₂Ph₂H), 127.26, 128.53, 128.58 (CH, Ph), 127.84, 130.46, 133.71 (C_q; C–CH₃, C–Ph and Ph). EI-MS, m/z (relative abundance): 656 (18), 655 (15), 654 (39), 653 (23), 652 (M⁺; 54), 651 (29), 650 (46), 636 (13), 635 (9), 634 (15), 411 (29), 410 (16), 409 (66), 408 (33), 407 ([M–C₅Me₂Ph₂H]⁺; 100), 406 (18), 405 (94), 393 (11), 391 (17), 390 (10), 389 (25), 371 (10), 369 (19), 367 (19), 365 (10), 246 (14), 245 ([C₅Me₂Ph₂H]⁺; 24), 244 (11), 229 (12), 228 (11), 215 (11), 165 (9). IR (KBr, cm⁻¹): 3056 (s), 3032 (s), 2978 (m), 2966 (m), 2922 (s), 2866 (m), 1684 (w), 1599 (m), 1576 (m), 1514 (m), 1504 (m), 1470 (s), 1452 (s), 1379 (m), 1303 (vw), 1183 (w), 1155 (m), 1105 (vw), 1077 (w), 1032 (w), 1006 (vw), 919 (vw), 852 (m), 843 (m), 818 (m), 764 (vs), 715 (m), 695 (vs), 670 (w), 648 (m), 638 (w), 611 (m), 585 (vw), 520 (vw), 500 (w), 418 (w). Calc. for C₃₈H₃₄Cl₂Zr: C, 69.91; H, 5.25. Found: C, 69.36; H, 5.39%.

3.7. Preparation of (η^5 -2,3-dimethyl-1,4-diphenylcyclopentadienyl)(η^5 -cyclopentadienyl)dichlorozirconium (**6**)

A mixture of solid dimethyldiphenylcyclopentadienyl lithium salt (0.436 g, 1.73 mmol) and solid cyclopentadienyltrichlorozirconium(dimethoxyethane) (0.610 g, 1.73 mmol) was cooled to $-50\text{ }^\circ\text{C}$ and 20 ml of toluene was added. The reaction mixture was stirred for 30 min at this temperature and then allowed to warm to room temperature. A resulting voluminous yellow slurry was refluxed for additional 14 h. The toluene was removed in vacuum and traces of 2,3-dimethyl-1,4-diphenylcyclopentadiene were sublimed off at $105\text{--}125\text{ }^\circ\text{C}/0.5$ mmHg from a solid residue. The residue was extracted with 80 ml of toluene and the formed suspension was filtered through cellite pad. A clear yellow filtrate was concentrated to ca. 30 ml, the product dissolved under boil, and

then the solution was slowly cooled, finally to $-18\text{ }^\circ\text{C}$. Slightly yellow microcrystals were isolated, washed with pentane and dried in vacuum. Yield 0.345 g (42%).

m.p. $250\text{ }^\circ\text{C}$. ^1H NMR (CDCl_3): 2.36 (s, 6H, Cp(CH₃)₂), 6.16 (s, 5H, CpH), 6.94 (s, 1H, CpMe₂Ph₂H), 7.14 (tt, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.5$, 2H, C(4)H, Ph), 7.41–7.45 (m, 4H, C(3)H, Ph), 7.47–7.51 (m, 4H, C(2)H, Ph). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): 13.69 (CpCH₃), 108.43 (CH, CpMe₂Ph₂H), 116.40 (CH, Cp), 128.01, 128.75, 129.04 (CH, Ph), 126.32, 130.78, 134.57 (C_q; C–CH₃, C–Ph and Ph). EI-MS, m/z (relative abundance): 476 (29), 475 (18), 474 (64), 473 (36), 472 (M⁺; 95), 471 (43), 470 (89), 411 (31), 410 (16), 409 (67), 408 (33), 407 ([M–Cp]⁺; 100), 406 (40), 405 (93), 369 (17), 368 (9), 367 (18), 366 (10), 365 (12), 329 (5), 245 ([C₅Me₂Ph₂H]⁺; 15), 229 (23), 228 (15), 227 ([CpZrCl₂]⁺; 19), 225 (15), 215 (13), 165 (9). IR (KBr, cm⁻¹): 3103 (s), 3075 (s), 3062 (s), 3033 (s), 2982 (m), 2958 (m), 2914 (s), 1599 (m), 1576 (w), 1512 (w), 1502 (w), 1471 (m), 1447 (s), 1381 (m), 1148 (w), 1109 (vw), 1074 (w), 1020 (m), 1014 (m), 934 (vw), 913 (vw), 851 (s), 818 (vs), 769 (vs), 764 (vs), 743 (w), 698 (vs), 670 (w), 656 (w), 648 (w), 613 (w), 585 (w), 532 (w), 461 (vw), 406 (vw). Calc. for C₂₄H₂₂Cl₂Zr: C, 61.00; H, 4.69. Found: C, 60.80; H, 4.73%.

3.8. X-ray crystallography

The red crystals of **4** were grown from toluene/hexane solution, the yellow crystals of **5** were obtained by pentane gas-phase transfer into a dichloromethane solution. All diffraction data were collected on a Nonius KappaCCD diffractometer. The structures were solved by direct methods (SIR-92 [25]) and refined by weighted full-matrix least-squares on F^2 (SHELXL97 [26]). All non-hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in calculated position. Relevant crystallographic data are collected in Table 4.

3.9. Ethene polymerization

A 250 ml Büchi glass autoclave equipped with a magnetic stirrer was filled with argon and toluene and the solution of methylalumoxane (10 wt% in toluene; Al:M = 10,000:1) was injected. After stirring at $20\text{ }^\circ\text{C}$ for 10 min, a solution of metallocene dichloride in toluene was injected (total volume of polymerization solution was 50 ml and concentration of metallocene dichloride was 2.5×10^{-6} M for all experiments). After preactivation for 10 min, the autoclave was pressurized with 4 bar of ethene for 30 min and stirred at 400 rpm. Finally, the autoclave was vented and the polymerization was quenched with 10% HCl in ethanol (80 ml). A precipitated polymer was stirred in acidified ethanol for 1 h, filtered, washed with water and ethanol, and dried in vacuum to constant weight.

Table 4

Crystallographic data, data collection and structure refinement data for compounds **4** and **5**^a

	4	5
Chemical formula	C ₃₈ H ₃₄ Cl ₂ Ti	C ₃₈ H ₃₄ Cl ₂ Zr
Molecular weight	609.45	652.77
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>T</i> (K)	293	150
<i>a</i> (Å)	17.7050(3)	17.6200(1)
<i>b</i> (Å)	15.3880(3)	15.4060(1)
<i>c</i> (Å)	22.4210(4)	22.4510(2)
α (°)	90.000	90.000
β (°)	96.7590(11)	96.9490(3)
γ (°)	90.000	90.000
<i>Z</i>	8	8
Crystal size (mm ³)	0.40 × 0.35 × 0.12	0.35 × 0.32 × 0.22
<i>d</i> _{calc} (g cm ⁻³)	1.335	1.433
μ (Mo K α) (mm ⁻¹)	0.485	0.567
<i>F</i> (000)	2544	2688
θ range (°)	2.99–25.02	1–27.5
<i>hkl</i> range	–21/21, –18/16, –26/26	–22/22, –19/19, –29/29
Diffraction collected	7289	11678
Parameters	747	747
<i>R</i> , <i>wR</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0436, 0.0989	0.0291, 0.0693
<i>R</i> , <i>wR</i> (all data)	0.0779, 0.1152	0.0386, 0.0746
<i>S</i>	1.029	1.030
ρ _{max,min} (e Å ⁻³)	0.255, –0.310	0.420, –0.587

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

4. Supplementary material

Crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (**4**: 215219, **5**: CCDC-215744). Copies of the data can be obtained free of charge upon application to The director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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