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New zirconocenes with 4,5,6,7-tetrahydroindene ligands. Synthesis and catalytic activity in the polymerization of ethylene and copolymerization of ethylene with hex-1-ene

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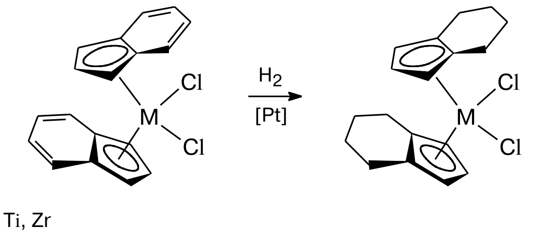
A series of symmetric and nonsymmetric tetrahydroindenyl zirconium complexes was obtained by the reaction of $ZrCl_4$ or $(CpTMS)ZrCl_3$ with lithium salts of the corresponding tetrahydroindenes. Activated with methylalumoxane, these complexes exhibit high activity in polymerization of ethylene (up to $6.8 \cdot 10^6$ g PE (mol Zr h)$^{-1}$), as well as in copolymerization of ethylene and hex-1-ene (up to $8.6 \cdot 10^6$ g PE (mol Zr h)$^{-1}$).

Key words: zirconocenes, 4,5,6,7-tetrahydroindene, polymerization, copolymerization, ethylene, hex-1-ene.

In 1980, it was shown[1] that zirconocene Cp_2ZrCl_2 activated with methylalumoxane (MAO) forms a catalytic system (Cp_2ZrCl_2—MAO), which exhibits considerably higher catalytic activity than the systems based on trimethylaluminum. This gave an additional impetus to the wider use of metallocene catalysts in polymerization of α-olefins in laboratory practice and industry.[2,3] The developers of new metallocene-type catalysts have set two goals: 1) to increase productivity of catalyst for decreasing the cost of production of polyolefins and 2) to use them for obtaining a series of polymers with improved physical properties (such as recyclability, mechanical and optical properties) through a fine control of molecular weight (M_w), molecular weight distribution (MWD), incorporation degree, and statistical distribution of a comonomer in the polymer chain, as well as a branching degree of the polymeric chain.[2,4,5]

In the work,[6] the authors reported the preparation of titanium and zirconium bis-η^5-tetrahydroindenyl complex dichlorides in 29% (Ti) and 37% (Zr) yields by the hydrogenation on the Adams catalyst of the corresponding indenyl derivatives (Ind_2MCl_2). At the present time, hydrogenation of indenyl precursors is the basic method for the preparation of IV group metal tetrahydroindenyl complexes, which are important representatives of catalysts of homogeneous polymerization of olefins[7,8] (Scheme 1).

Scheme 1



Hydrogenated metallocene complexes possess favorable steric and electron properties, as well as are more stables to hydrolysis.[9,10] As a rule, hydrogenation of the benzene part is the last step of the synthesis of tetrahydroindenyl complexes. These reactions frequently give low yields, require expensive autoclave equipment and compliance with fire safety measures. Apart from that, it was shown earlier that the hydrogenation of IVb group metal metallocene dichloride complexes can result in the formation of side products, such as hydride and low-valence complexes.[11]

Thus, the development of an alternative method for the synthesis of tetrahydroindenyl ligands is an actual problem, the solution of which will make it possible to considerably broaden the scope of synthetically available tetrahydroindenyl metallocenes. By the present moment, only

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a limited amount of synthetic approaches to tetrahydroindenyl ligands have been described.[12—16]

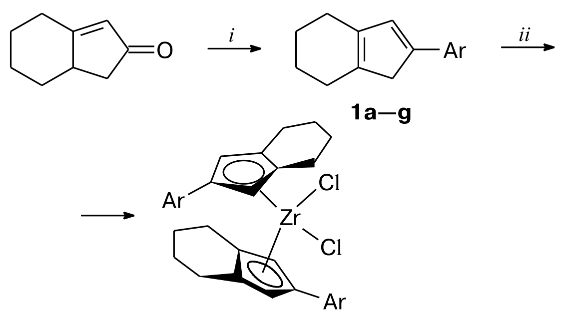
The purpose of the present work is the synthesis of new zirconium complexes with substituted tetrahydroindenyl ligands, bearing aryl substituents at positions 1 and 2 of tetrahydroindene ($IndH_4$). Such complexes cannot be obtained in the individual state by hydrogenation because of the low selectivity of the Adams catalyst, which gives a mixture of products of reduction of both the indenyl fragment and the aromatic substituent. It should be noted that several examples of the synthesis of symmetric 2-aryl-substituted tetrahydroindenyl metallocenes have been described earlier,[17] but no data on the synthesis of their nonsymmetric analogues are available. This work is a continuation of our studies on the development of metallocene catalysts of polymerization of olefins.[18—21]

Results and Discussion

A synthetic approach to zirconium complexes with substituted tetrahydroindenyl units is given in Scheme 2. The starting 2*H*-3,3a,4,5,6,7-hexahydroinden-2-one,[22] 2,3,4,5,6,7-hexahydroind-8(9)-en-l-one, and 2-methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-l-one[23] were synthesized according to the procedures described in the literature. 2-Aryl-substituted ligands **1a—g** were obtained in three steps from 2*H*-3,3a,4,5,6,7-hexahydroinden-2-one (Scheme 2). Its reaction with arylmagnesium bromides led to the corresponding allylic alcohols, which without isolation were dehydrated under mild conditions with a hydrogen chloride ethereal solution. Since tetrahydroindenes **1a—g** can readily undergo polymerization, to obtain their high yields it is important to maintain the temperature low and carry out the dehydration over a short time. It is also important to note that the reaction conditions suggested allow one to obtain only one of possible isomeric dienes **1a—g** and avoid migration of the double bonds of the cyclopentadiene ring. The deprotonation of tetrahydroindenes **1a—g** with a small excess of Bu^nLi leads to the formation of the corresponding lithium salts in a total three-step yield from 50 to 90%. The reaction of the lithium salts with $ZrCl_4 \cdot 2THF$ in ether in the molar ratio of 2 : 1 leads to the corresponding metallocenes **2a—g** in high yields.

Synthesis of 1-aryl-substituted tetrahydroindenes is given in Scheme 3. 1-Phenyltetrahydroindene (**1h**) was obtained in two steps from 2,3,4,5,6,7-hexahydroind-8(9)-en-l-one. Its treatment with phenylmagnesium bromide leads to the corresponding allylic alcohol, which was involved in the second step of dehydration without additional purification. The dehydration was carried out for 20 min under mild conditions with a catalytic amount of HCl in a solution of the alcohol in diethyl ether at ~20 °C. The target product **1h** was obtained in 52% yield. 2-Methyl-1-tolyltetrahydroindene (**1i**) was obtained in one step from 2-methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-l-one upon treatment with *p*-tolyllithium with subsequent addition of HCl in diethyl ether in 81% yield.

Scheme 2

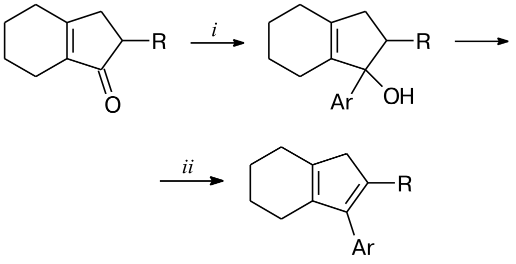


2a—g

1, **2:** Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$MeCHC_6H_4$ (**c**), 4-$Bu^tC_6H_4$ (**d**), 4-FC_6H_4 (**e**), 4-$MeOC_6H_4$ (**f**), 2-$MeOC_6H_4$ (**g**)

Reagents: *i.* 1) $ArMgBr/Et_2O$, 2) HCl/Et_2O; *ii.* 1) Bu^nLi, 2) $ZrCl_4(THF)_2$.

Scheme 3



1h,i

1: Ar = Ph (**h**), 4-MeC_6H_4 (**i**); R = H (**h**), Me (**i**); M = MgBr (**h**), Li (**i**)

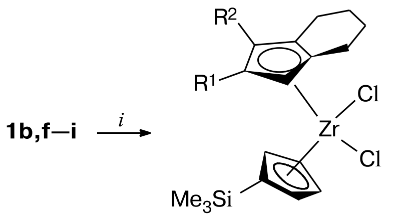
Reagents: *i.* 1) ArM, 2) H^+; *ii.* HCl, H_2O.

Indenes **1b**, **f—i** were converted to the corresponding lithium salts by treatment with a slight excess of Bu^nLi in diethyl ether (Scheme 4). The reaction of the lithium salts with $(TMSC_5H_4)ZrCl_3$ (synthesized according to the procedure described earlier[24]) in toluene in the ratio of 1 : 1 gave the corresponding complexes **2h—l** in high yields. All the zirconocenes **2a—l** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis.

The catalytic studies in the reactions of polymerization of ethylene and copolymerization of ethylene with hex-1-ene were carried out by the specialists of the LG Chem company in the Research Center in Daejeon, South Korea. As a result of these studies, an international patent has been obtained.[25] In the present work, we report the data on the catalytic systems demonstrated the highest activity, which were given in the patent.[25]

To study the influence of catalyst structure on the catalytic activity in polymerization of ethylene and copoly-

Scheme 4



2h—l

Reagents: *i*. 1) $\mathrm{Bu^nLi}$, 2) $(\mathrm{TMSC_5H_4})\mathrm{ZrCl_3}$.

Compound	R^1	R^2
2h	H	Ph
2i	Me	$4\text{-}\mathrm{MeC_6H_4}$
2j	$4\text{-}\mathrm{MeC_6H_4}$	H
2k	$4\text{-}\mathrm{MeOC_6H_4}$	H
2l	$2\text{-}\mathrm{MeOC_6H_4}$	H

merization of ethylene and hex-1-ene, we carried out a series of catalytic experiments (Table 1). Based on the given data, a conclusion can be drawn that the size of the substituent at position 2 of tetrahydroindenyl ligand considerably affect the value of the weight average molecular mass of a polymer obtained. As the size of substituents increases in the order H (**2h**) < methyl (**2i**) < *p*-tolyl (**2j**) ≈ ≈ 4-methoxyphenyl (**2k**), the weight average molecular mass (M_w) decreases from 71000 to 30000. It should also be noted that the introduction of a substituent at position 2 of tetrahydroindenyl ligand leads to a considerable decrease in the MWD (molecular weight distribution). Thus, the polymers obtained on the unsubstituted catalyst **2h** (entries *1* and *5*) are characterized by about twice as high values of MWD than the polymers synthesized using 2-aryl-substituted zirconocenes **2j** and **2k** (entries *3*, *4*, *7*, and *8*). A comparison of the results of entries *1—4* and *5—8* also shows that the addition into the polymerization mixture of hex-1-ene increases activity of the catalysts **2h**, **2i**, and **2k**. In this case, a decrease in the weight average molecular mass of polymers (M_w) and an increase in the MWD are observed. Conversely, in the case of catalyst **2j** the introduction of hex-1-ene leads to the decrease in activity, weight average molecular mass of the polymer, and molecular weight distribution.

In conclusion, we developed an efficient method for the synthesis of 1- and 2-aryl-substituted tetrahydroindenes (**1a—i**) and their symmetric (**2a—g**) and nonsymmetric (**2h—l**) complexes with zirconium. Complexes **2h—k** exhibit high catalytic activity in polymerization of ethylene ($6.8 \cdot 10^6$ g PE (mol zirconocene h)$^{-1}$ for the system **2i**—MAO and **2k**—MAO), as well as in the copolymerization reaction of ethylene with hex-1-ene ($8.6 \cdot 10^6$ g copolymer (mol zirconocene h)$^{-1}$ for the system **2i**—MAO).

Experimental

All the manipulations were carried out under pure argon using standard Schlenk technique. Tetrahydrofuran, hexane, and toluene were distilled over the system sodium—benzophenone. Dichloromethane was distilled over calcium hydride. Aryl bromides, dicyclopentadiene, a solution of $\mathrm{Bu^nLi}$, chlorotrimethylsilane, a solution of hydrogen chloride in diethyl ether, and zirconium(IV) salts were purchased from Aldrich, Fluka, ABCR, Merck, and Acros and used without additional purification. ^{1}H (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on an AVANCE 400 spectrometer in a solution in $\mathrm{CDCl_3}$. Elemental analysis was carried out using a Carlo Erba E1108 CHNC-O analyzer.

Synthesis of arylmagnesium bromides (general procedure). Magnesium (2.4 g, 0.1 mol) was placed into a two-neckel flask (250 mL) equipped with a reflux condenser and anhydrous diethyl ether (100 mL) was added. Without stirring, a small amount (~10%) of aryl bromide and 1,2-dibromoethane (0.2 mL) for activation of magnesium were added to the solution. After beginning of the reaction, the solution was stirred and the rest of aryl bromide (a total of 0.1 mol in diethyl ether (20 mL)) was added over 30 min, then the reaction mixture was refluxed for 2 h. After cooling the mixture to ~20 °C, the solution was transferred into another flask, followed by the addition of diethyl ether to a total volume of 150 mL. The concentration of Grignard reagents was determined by titration. This procedure was used to obtain phenylmagnesium bromide, *p*-tolylmagnesium bromide, 4-isopropylphenylmagnesium bromide, 4-*tert*-butylphenylmagnesium bromide, 4-fluorophenylmagnesium bromide, 4-methoxyphenylmagnesium bromide, 2-methoxyphenylmagnesium bromide.

Synthesis of 2-aryltetrahydroindenes (general procedure). A solution of arylmagnesium bromide (1 equiv.) was added dropwise to a solution of 4,5,6,7-tetrahydroinden-2-one (10 g, 0.074 mol) in anhydrous diethyl ether (100 mL) cooled to –20 °C over 20 min. Then, the cooling bath was removed and the mixture was

Table 1. Results of catalytic tests of zirconocenes

Entries	Monomers	Metallocene	Activity /kg PE (mmol zirconocene h)$^{-1}$	M_w/g mol^{-1}	MWD
1	$\mathrm{C_2H_4}$	**2h**	4.5	71000	8.5
2	$\mathrm{C_2H_4}$	**2i**	6.8	53000	4.2
3	$\mathrm{C_2H_4}$	**2j**	6.3	30000	4.7
4	$\mathrm{C_2H_4}$	**2k**	6.8	34000	4.4
5	$\mathrm{C_2H_4+C_6H_{12}}$	**2h**	6.3	47000	10.3
6	$\mathrm{C_2H_4+C_6H_{12}}$	**2i**	8.6	26000	7.6
7	$\mathrm{C_2H_4+C_6H_{12}}$	**2j**	6.0	17000	4.0
8	$\mathrm{C_2H_4+C_6H_{12}}$	**2k**	7.7	14000	5.6

stirred for 8 h. After this, the reaction mixture was cooled to –10 °C, followed by the addition of a 2.0 *M* solution of hydrogen chloride (41 mL, 1.11 equiv.) in diethyl ether. After 15 min, the mixture was poured into water (200 mL), the organic layer was separated, whereas the aqueous layer was extracted with diethyl ether. The combined organic fractions were dried with sodium sulfate. The solvent was removed at reduced pressure. The product was purified by column chromatography on silica gel (eluent *n*-hexane).

2-Phenyl-4,5,6,7-tetrahydroindene (1a). A white crystalline compound, the yield was 9.2 g (64%). ^{1}H NMR (CDCl$_3$), δ: 1.67—1.78 (m, 4 H); 2.25—2.33 (m, 2 H); 2.33—2.42 (m, 2 H); 3.24 (s, 2 H); 6.66 (s, 1 H); 7.14 (t, 1 H, *J* = 7.32 Hz); 7.28 (t, 2 H, *J* = 7.69 Hz); 7.45 (d, 2 H, *J* = 8.30 Hz). ^{13}C NMR (CDCl$_3$), δ: 23.03, 23.22, 24.39, 25.47, 43.14, 124.57, 125.98, 128.45, 129.47, 136.62, 138.88, 139.20, 143.14. Found (%): C, 91.96; H, 8.04. $C_{15}H_{16}$. Calculated (%): C, 91.78; H, 8.22.

2-(*p*-Tolyl)-4,5,6,7-tetrahydroindene (1b). A white powder, the yield was 10.3 g (66%). ^{1}H NMR (CDCl$_3$), δ: 1.04 (d, 3 H, *J* = 6.85 Hz); 1.23—1.38 (m, 1 H); 1.43—1.60 (m, 1 H); 1.66—1.90 (m, 2 H); 2.09—2.27 (m, 4 H); 2.38 (s, 3 H); 3.27—3.38 (m, 1 H); 5.54 (d, 1 H, *J* = 2.57 Hz); 7.19 (d, 2 H, *J* = 8.31 Hz); 7.23 (d, 2 H, *J* = 8.31 Hz). ^{13}C NMR (CDCl$_3$), δ: 20.42, 20.79, 22.35, 24.83, 24.85, 36.29, 38.87, 127.54, 128.38, 128.49, 135.58, 142.51, 145.22, 147.72, 153.99. Found (%): C, 91.30; H, 8.58. $C_{16}H_{18}$. Calculated (%): C, 91.37; H, 8.63.

2-(4-Isopropylphenyl)-4,5,6,7-tetrahydroindene (1c). Pale yellow crystals, the yield was 9.0 g (51%). ^{1}H NMR (CDCl$_3$), δ: 1.29 (d, 6 H); 1.76 (d, 4 H); 2.35 (d, 4 H); 2.92 (d, 1 H); 3.27 (s, 1 H); 6.65 (s, 1 H); 7.20 (d, 2 H); 7.42 (d, 2 H). ^{13}C NMR (CDCl$_3$), δ: 22.65, 22.85, 23.55, 24.02, 25.08, 33.37, 42.79, 124.21, 126.12, 128.29, 133.96, 138.25, 138.46, 142.82, 146.32. Found (%): C, 90.63; H, 9.27. $C_{18}H_{22}$. Calculated (%): C, 90.70; H, 9.30.

2-(4-*tert*-Butylphenyl)-4,5,6,7-tetrahydroindene (1d). Pale yellow crystals, the yield was 8.0 g (43%). ^{1}H NMR (CDCl$_3$), δ: 1.37 (s, 9 H); 1.77 (d, 4 H); 2.37 (d, 4 H); 3.28 (br.s, 2 H); 6.66 (s, 1 H); 7.38 (d, 2 H, *J* = 8.56 Hz); 7.44 (d, 2 H, *J* = 8.56 Hz). ^{13}C NMR (CDCl$_3$), δ: 22.66, 22.86, 24.03, 25.10, 30.93, 34.06, 42.78, 123.96, 124.98, 128.39, 133.57, 138.29, 138.28, 142.72, 148.55. Found (%): C, 90.39; H, 9.60. $C_{19}H_{24}$. Calculated (%): C, 90.42; H, 9.58.

2-(4-Fluorophenyl)-4,5,6,7-tetrahydroindene (1e). A white powder, the yield was 7.6 g (48%). ^{1}H NMR (CDCl$_3$), δ: 1.76 (dt, 4 H, *J* = 6.02 Hz, *J* = 2.92 Hz); 2.27—2.36 (m, 2 H); 2.36—2.43 (m, 2 H); 3.23 (d, 2 H, *J* = 1.10 Hz); 6.61 (s, 1 H); 6.96—7.06 (m, 2 H); 7.38—7.49 (m, 2 H). ^{13}C NMR (CDCl$_3$), δ: 22.62, 22.81, 23.98, 25.04, 42.86, 114.90 (d, *J* = 21.47); 125.53, 125.60, 128.77, 132.53 (d, *J* = 3.45); 138.58 (d, *J* = 15.34), 141.66, 161.04 (d, *J* = 244.98). Found (%): C, 83.97; H, 7.01. $C_{15}H_{15}F$. Calculated (%): C, 84.08; H, 7.06.

2-(4-Methoxyphenyl)-4,5,6,7-tetrahydroindene (1f). A white powder, the yield was 12.1 g (72%). ^{1}H NMR (CDCl$_3$), δ: 1.47 (d, 2 H); 1.86 (d, 2 H); 2.33 (d, 2 H); 2.56 (d, 2 H); 3.49 (s, 2 H); 3.82 (s, 3 H); 6.61 (s, 1 H); 6.84 (d, 2 H); 7.30 (d, 2 H). ^{13}C NMR (CDCl$_3$), δ: 22.28, 22.34, 30.00, 33.56, 48.57, 55.29, 114.01, 127.41, 128.98, 131.81, 133.69, 139.67, 150.33, 159.05. Found (%): C, 84.82; H, 8.12. $C_{16}H_{18}O$. Calculated (%): C, 84.91; H, 8.02.

2-(2-Methoxyphenyl)-4,5,6,7-tetrahydroindene (1g). A white powder, the yield was 15.6 g (93%). ^{1}H NMR (CDCl$_3$), δ: 1.78 (d, 2 H); 1.96 (d, 2 H); 2.19 (d, 1 H); 2.32 (d, 1 H); 2.53 (d, 2 H); 3.55 (d, 2 H); 3.87 (d, 3 H); 5.94 (d, 1 H); 6.96 (td, 1 H, *J* = 7.51 Hz, *J* = 1.22 Hz); 7.04 (d, 1 H, *J* = 8.30 Hz); 7.19 (dt, 2 H, *J* = 7.53 Hz, *J* = 5.77 Hz, *J* = 1.83 Hz); 7.49 (t, 1 H, *J* = 7.72 Hz). ^{13}C NMR (CDCl$_3$), δ: 21.70, 21.90, 23.58, 23.76, 49.82, 54.67, 110.61, 115.19, 120.29, 127.88, 128.36, 130.38, 130.79, 133.37, 143.78, 155.18. Found (%): C, 84.84; H, 8.09. $C_{16}H_{18}O$. Calculated (%): C, 84.91; H, 8.02.

1-Phenyl-4,5,6,7-tetrahydroindene (1h) was obtained according to the general procedure from 4,5,6,7-tetrahydroinden-1-one, the yield was 5.6 g (52%). ^{1}H NMR (CDCl$_3$), δ: 1.62—1.74 (m, 4 H); 2.54—2.62 (m, 2 H); 2.62—2.67 (m, 2 H); 2.79—2.86 (m, 2 H); 5.60 (w.sh, 1 H); 7.24 (t, 1 H, *J* = 7.23 Hz); 7.36 (t, 2 H, *J* = 7.81 Hz); 7.41 (d, 2 H, *J* = 8.14 Hz). ^{13}C NMR (CDCl$_3$), δ: 22.80, 25.12, 25.64, 27.26, 33.29, 116.58, 126.50, 127.42, 128.14, 137.04, 137.95, 138.22, 147.16. Found (%): C, 91.74; H, 8.26. $C_{15}H_{16}$. Calculated (%): C, 91.78; H, 8.22.

2-Methyl-1-(*p*-tolyl)-4,5,6,7-tetrahydroindene (1i). A solution of Bu^nLi (13.3 mL, 2.5 *M*) was added to a solution of 4-bromotoluene (5.69 g, 0.033 mol) in anhydrous THF cooled to –80 °C at such a rate that to keep the temperature of the reaction mixture below –60 °C. The reaction mixture was stirred for another 1 h at –80 °C, followed by the addition of 2-methyl-4,5,6,7-tetrahydroindan-1-one, the cooling bath was removed. When the mixture warmed-up to ~20 °C, it was diluted by a solution of hydrochloric acid (2 mL, 2.0 *M*). THF was evaporated at reduced pressure, dichloromethane (100 mL) was added to the residue. The organic layer was separated, whereas the aqueous layer was extracted twice with dichloromethane. The combined organic layer was dried with Na_2SO_4, the solvent was removed on a rotary evaporator. The product was isolated using column chromatography on silica gel (eluent dichloromethane). The yield was 6 g (81%) of pure compound obtained as pale yellow crystals.

^{1}H NMR (CDCl$_3$), δ: 1.5 (d, 1 H); 1.55 (d, 1 H); 1.79 (d, 2 H); 2.02 (s, 3 H); 2.17 (d, 4 H); 2.39 (d, 3 H); 3.34 (s, 1 H); 5.54 (s, 1 H); 7.14—7.29 (m, 4 H). ^{13}C NMR (CDCl$_3$), δ: 20.42, 20.79, 22.35, 24.83, 36.29, 38.87, 115.57, 127.54, 128.27, 128.38, 128.49, 135.58, 142.51, 145.22. Found (%): C, 91.09; H, 8.91. $C_{17}H_{20}$. Calculated (%): C, 91.01; H, 8.99.

Bis(2-aryl-4,5,6,7-tetrahydroindenyl)zirconium dichlorides (general procedure). Butyllithium (5.2 mL, 2.5 *M* solution in hexane) was added dropwise to a solution of 2-aryl-4,5,6,7-tetrahydroindene (13 mmol) in anhydrous diethyl ether (70 mL) at –20 °C. The solution was warmed-up to ~20 °C and stirred overnight. The reagent $ZrCl_4(THF)_2$ (4.4 g, 12 mmol) was added to the lithium salt obtained, the mixture was stirred for 8 h. The solvents were evaporated at reduced pressure, the residue was diluted with anhydrous toluene (50 mL) and the mixture was heated to 80—90 °C. The resulting mixture was filtered through celite, the filtrate was concentrated and diluted with anhydrous hexane (10 mL). Then, the solution was placed into a freezer to crystallize the product. The crystals formed were collected by filtration, washed several times with anhydrous hexane, and dried *in vacuo* (~1 Torr).

Bis(2-phenyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (2a). A grey microcrystalline powder, the yield was 0.970 g (27%). ^{1}H NMR (CDCl$_3$), δ: 1.44 (d, 4 H); 1.87 (d, 4 H); 2.33 (d, 8 H); 6.24 (s, 4 H); 7.23—7.41 (m, 10 H). ^{13}C NMR (CDCl$_3$), δ: 21.98, 23.83, 113.63, 123.97, 125.23, 127.25, 128.92, 130.80, 133.33. Found (%): C, 64.31; H, 5.96. $C_{30}H_{30}Cl_2Zr$. Calculated (%): C, 65.19; H, 5.47.

Bis[2-(*p*-tolyl)-4,5,6,7-tetrahydroindenyl]zirconium dichloride (2b). A grey microcrystalline powder, the yield was 1.17 g

(31%). ^{1}H NMR (CDCl$_3$), δ: 1.38—1.51 (m, 4 H); 1.80—1.95 (m, 4 H); 2.23—2.34 (m, 4 H); 2.37 (s, 6 H); 2.39—2.50 (m, 4 H); 6.18 (s, 4 H); 7.16 (d, 4 H, *J* = 7.81 Hz); 7.27 (d, 4 H, *J* = 8.30 Hz). ^{13}C NMR (CDCl$_3$), δ: 21.18, 22.04, 22.60, 23.92, 31.54, 113.27, 124.60, 125.19, 129.51, 130.51, 130.67, 137.03. Found (%): C, 66.51; H, 6.02. $C_{32}H_{36}Cl_2Zr$. Calculated (%): C, 66.18; H, 5.90.

Bis[2-(4-isopropylphenyl)-4,5,6,7-tetrahydroindenyl]zirconium dichloride (2c). A yellow microcrystalline powder, the yield was 1.41 g (34%). ^{1}H NMR (CDCl$_3$), δ: 1.26 (d, 12 H, *J* = 6.91 Hz); 1.36—1.45 (m, 4 H); 1.78—1.87 (m, 4 H); 2.17—2.24 (m, 4 H); 2.24—2.32 (m, 4 H); 2.92 (septet, 2 H, *J* = 6.92 Hz); 6.26 (s, 4 H); 7.24 (d, 4 H, *J* = 8.22 Hz); 7.36 (d, 4 H, *J* = 8.22 Hz). ^{13}C NMR (CDCl$_3$), δ: 22.04, 23.68, 24.02, 33.87, 113.32, 124.00, 125.30, 126.94, 130.49, 130.73, 148.27. Found (%): C, 67.97; H, 6.81. $C_{36}H_{42}Cl_2Zr$. Calculated (%): C, 67.89; H, 6.65.

Bis[2-(4-*tert*-butylphenyl)-4,5,6,7-tetrahydroindenyl]zirconium dichloride (2d). Large yellow crystals, the yield was 1.25 g (29%). ^{1}H NMR (CDCl$_3$), δ: 1.33 (s, 18 H); 1.34—1.42 (m, 4 H); 1.77—1.86 (m, 4 H); 2.14—2.27 (m, 8 H); 6.27 (s, 4 H); 7.38 (d, 4 H, *J* = 8.39 Hz); 7.40 (d, 4 H, *J* = 8.39 Hz). ^{13}C NMR (CDCl$_3$), δ: 22.01, 23.59, 31.33, 34.63, 113.32, 123.72, 125.02, 125.79, 130.25, 130.49, 150.54. Found (%): C, 69.17; H, 7.11. $C_{38}H_{46}Cl_2Zr$, Calculated (%): C, 68.64; H, 6.97.

Bis[2-(4-fluorophenyl)-4,5,6,7-tetrahydroindenyl]zirconium dichloride (2e). A pale yellow microcrystalline powder, the yield was 1.53 g (40%). ^{1}H NMR (CDCl$_3$), δ: 1.42—1.52 (m, 4 H); 1.80—1.88 (m, 4 H); 2.31—2.40 (m, 4 H); 2.42—2.50 (m, 4 H); 6.20 (s, 4 H); 7.02 (t, 4 H, *J* = 8.59 Hz); 7.30 (dd, 4 H, *J* = 8.80 Hz, *J* = 5.18 Hz). ^{13}C NMR (CDCl$_3$), δ: 22.04, 24.04, 113.03, 115.82 (d, *J* = 21.01 Hz); 123.68, 126.92 (d, *J* = 7.74 Hz); 129.46 (d, *J* = = 3.21 Hz); 130.86, 162.01 (d, *J* = 247.68 Hz). Found (%): C, 61.44; H, 4.85. $C_{30}H_{28}F_2Cl_2Zr$. Calculated (%): C, 61.21; H, 4.79.

Bis[2-(4-methoxyphenyl)-4,5,6,7-tetrahydroindenyl]zirconium dichloride (2f). Bright yellow crystals, the yield was 1.87 g (47%). ^{1}H NMR (CDCl$_3$), δ: 1.46 (d, 4 H); 1.85 (d, 4 H); 2.33 (d, 4 H); 2.45 (d, 4 H); 3.83 (s, 6 H); 6.16 (s, 4 H); 6.88 (d, 4 H); 7.30 (d, 4 H). ^{13}C NMR (CDCl$_3$), δ: 22.08, 23.97, 55.30, 112.59, 114.18, 124.85, 126.15, 126.56, 130.29, 158.92. Found (%): C, 62.99; H, 5.77. $C_{32}H_{34}Cl_2O_2Zr$. Calculated (%): C, 62.73; H, 5.59.

Bis[2-(2-methoxyphenyl)-4,5,6,7-tetrahydroindenyl]zirconium dichloride (2g). A yellow microcrystalline powder, the yield was 1.71 g (43%). ^{1}H NMR (CDCl$_3$), δ: 1.45—1.59 (m, 4 H); 1.96—2.11 (m, 4 H); 2.32—2.44 (m, 4 H); 2.55—2.70 (m, 4 H); 3.92 (s, 6 H); 6.27 (s, 4 H); 6.95 (td, 2 H, *J* = 7.52 Hz, *J* = 1.22 Hz); 7.00 (d, 2 H, *J* = 8.31 Hz); 7.18 (dt, 2 H, *J* = 7.58 Hz, *J* = 5.78 Hz, *J* = 1.83 Hz); 7.29 (t, 2 H, *J* = 7.76 Hz). ^{13}C NMR (CDCl$_3$), δ: 21.70, 23.58, 54.67, 110.61, 115.19, 115.34, 120.29, 121.27, 122.43, 127.88, 128.36, 130.38, 155.18. Found (%): C, 62.90; H, 5.83. $C_{32}H_{34}Cl_2O_2Zr$. Calculated (%): C, 62.73; H, 5.59.

Bis(trimethylsilyl)cyclopentadiene. Cyclopentadiene dimer was decomposed at 160 °C. Butyllithium (2.5 *M* solution in hexane, 121 mL, 303 mmol,) and diethyl ether (100 mL) were placed into a 1-L flask. The solution was cooled to −5 °C, followed by a dropwise addition of cyclopentadiene (20 g, 303 mmol) and stirring for 18 h. All the volatile compounds were removed at reduced pressure. The residue was washed thrice with diethyl ether and dried *in vacuo*, using an oil pump. The yield of cyclopentadiene lithium salt was 21.3 g (293 mmol). This salt was dissolved in THF (150 mL), and trimethylsilyl chloride (50 mL) was slowly added at 0 °C. The reaction mixture was stirred overnight at ~20 °C, then water (100 mL) and diethyl ether (200 mL) were added. The organic layer was separated and dried with Na_2SO_4, the solvent was removed at reduced pressure. The product was distilled to obtain trimethylsilylcyclopentadiene (21.4 g) as a colorless liquid (b.p. 57—61 °C at 30 Torr). This compound was dissolved in diethyl ether (150 mL) and Bu^{n}Li (2.5 *M* solution in hexane, 62.5 mL) was added. The mixture was stirred over night, the solvents were removed at reduced pressure, the residue was dissolved in THF (100 mL). The solution was cooled to −80 °C and trimethylsilyl chloride (16.8 g, 155 mmol) was added. The reaction mixture was allowed to warm-up to ~20 °C (over about 1 h) and treated with little methanol and hydrochloric acid, and then poured into water. The product was extracted with hexane (3×100 mL). The combined organic layer was dried with magnesium sulfate. The evaporation of the solvent at reduced pressure gave the product (27.7 g, 40%) as a pale yellow oil. The product was a mixture of isomers. It was used in subsequent syntheses without additional purification.

(Trimethylsilylcyclopentadienyl)zirconium trichloride. Zirconium(IV) chloride (20.9 g, 90 mmol) was suspended in anhydrous toluene (450 mL). A mixture of isomers of bis(trimethylsilyl)cyclopentadiene (18.9 g, 90 mmol) was added to the suspension obtained and slowly heated to 100 °C. Then, the reaction mixture was stirred at this temperature overnight and filtered. The mother liquor obtained was placed into a freezer (−30 °C). A precipitate formed was collected by filtration, washed with hexane, and dried *in vacuo*, using an oil pump. The yield was 18.3 g (63%). ^{1}H NMR (CDCl$_3$), δ: 6.98 (d, 2 H); 6.94 (d, 2 H); 0.35 (s, 9 H).

(Aryl-4,5,6,7-tetrahydroindenyl)(trimethylsilylcyclopentadienyl)zirconium dichlorides (general procedure). Butyllithium (2.4 mL, 2.5 *M* solution in hexane) was added dropwise to a solution of aryl-4,5,6,7-tetrahydroindene (6 mmol) in anhydrous diethyl ether (40 mL) at −20 °C. Then, the solution was heated to ~20 °C and stirred for 8 h. Diethyl ether was removed at reduced pressure, toluene (40 mL) and (TMSC$_5$H$_4$)ZrCl$_3$ (1.8 g, 0.9 equiv.) were added to the residue. The reaction mixture was heated to 100 °C and stirred overnight. The resulting mixture was filtered through celite, the filtrate was concentrated to 10 mL. The solution obtained was placed into a freezer to crystallize the product. The crystals formed were collected by filtration, washed with anhydrous hexane several times and dried *in vacuo*, using an oil pump.

(1-Phenyl-4,5,6,7-tetrahydroindenyl)(trimethylsilylcyclopentadienyl)zirconium dichloride (2h). A yellow microcrystalline powder, the yield was 1.28 g (43%). ^{1}H NMR (CDCl$_3$), δ: 0.25 (s, 9 H); 1.42—1.58 (m, 1 H); 1.63—1.74 (m, 2 H); 1.93—2.03 (m, 1 H); 2.44—2.59 (m, 2 H); 2.92—3.03 (m, 1 H); 3.10—3.23 (m, 1 H); 5.73 (d, 1 H, *J* = 3.29 Hz); 5.87—5.96 (m, 1 H); 6.06—6.15 (m, 1 H); 6.35—6.41 (m, 1 H); 6.41—6.44 (m, 1 H); 6.72 (d, 1 H, *J* = 3.29 Hz); 7.27 (t, 1 H, *J* = 7.24 Hz); 7.31 (d, 2 H, *J* = 7.65 Hz); 7.38 (t, 2 H, *J* = 7.48 Hz). ^{13}C NMR (CDCl$_3$), δ: 0.00, 21.39, 22.75, 24.62, 25.18, 108.18, 110.87, 113.35, 119.15, 121.65, 124.53, 125.52, 127.43, 127.62, 128.78, 132.06, 134.04. Found (%): C, 56.00; H, 5.84. $C_{23}H_{28}Cl_2SiZr$. Calculated (%): C, 55.84; H, 5.71.

[2-Methyl-1-(*p*-tolyl)-4,5,6,7-tetrahydroindenyl](trimethylsilylcyclopentadienyl)zirconium dichloride (2i). A yellow microcrystalline powder, the yield was 0.75 g (24%). ^{1}H NMR (CDCl$_3$), δ: 0.26 (s, 9 H); 1.37—1.51 (m, 1 H); 1.51—1.58 (m, 1 H); 1.58—1.67 (m, 1 H); 1.69—1.80 (m, 1 H); 2.20 (s, 3 H); 2.22—2.26 (m, 1 H); 2.31 (s, 3 H); 2.47—2.59 (m, 1 H); 2.60—2.68 (m, 1 H); 2.93—3.05 (m, 1 H); 5.94 (br.s, 1 H); 6.06—6.10 (m, 1 H); 6.21—6.25 (m, 1 H); 6.46—6.50 (m, 2 H); 7.11 (d, 2 H, *J* = 8.14 Hz); 7.14 (d, 2 H, *J* = 8.14 Hz). ^{13}C NMR (CDCl$_3$), δ: 0.19, 16.72, 21.41, 22.67, 23.24, 25.01, 25.95, 111.37, 115.06, 116.27, 124.25, 125.67, 126.12, 126.23, 129.27, 130.43, 131.49, 135.30, 137.33. Found (%): C, 57.59; H, 6.23. $C_{25}H_{32}Cl_2SiZr$. Calculated (%): C, 57.44; H, 6.17.

[2-(*p*-Tolyl)-4,5,6,7-tetrahydroindenyl](trimethylsilylcyclopentadienyl)zirconium dichloride (2j). A yellow microcrystalline powder, the yield was 1.37 g (45%). ^{1}H NMR (CDCl$_3$), δ: 0.17 (s, 9 H); 1.48—1.59 (m, 2 H); 1.83—1.94 (m, 2 H); 2.32 (s, 3 H); 2.46—2.58 (m, 2 H); 2.72— 2.84 (m, 2 H); 5.94 (t, 2 H, J = 2.43 Hz); 6.23 (br.s, 2 H); 6.32 (t, 2 H, J = 2.47 Hz); 7.18 (d, 2 H, J = 8.14 Hz); 7.37 (d, 2 H, J = 8.14 Hz). ^{13}C NMR (CDCl$_3$), δ: –0.09, 21.21, 22.08, 24.60, 108.73, 117.62, 124.89, 125.17, 126.17, 128.32, 129.78, 131.12, 132.56, 137.68. Found (%): C, 56.95; H, 6.01. $C_{24}H_{30}Cl_2SiZr$. Calculated (%): C, 56.66; H, 5.94.

[2-(4-Methoxyphenyl)-4,5,6,7-tetrahydroindenyl](trimethylsilylcyclopentadienyl)zirconium dichloride (2k). A yellow microcrystalline powder, the yield was 1.61 g (51%). ^{1}H NMR (CDCl$_3$), δ: 0.27 (s, 9 H); 1.63 (d, 2 H); 2.02 (d, 2 H); 2.63 (d, 2 H); 2.89 (d, 2 H); 4.00 (s, 3 H); 6.03 (d, 2 H); 6.41 (d, 2 H); 6.54 (d, 1 H); 7.08 (d, 2 H); 7.33 (d, 2 H); 7.58 (d, 1 H). ^{13}C NMR (CDCl$_3$), δ: 0.50, 21.72, 24.14, 54.72, 111.02, 111.34, 117.30, 120.77, 122.64, 124.62, 127.34, 128.46, 132.21, 155.27. Found (%): C, 62.99; H, 5.77. $C_{32}H_{34}Cl_2O_2Zr$. Calculated (%): C, 62.73; H, 5.59. Found (%): C, 55.31; H, 5.88. $C_{24}H_{30}Cl_2OSiZr$. Calculated (%): C, 54.94; H, 5.76.

[2-(2-Methoxyphenyl)-4,5,6,7-tetrahydroindenyl](trimethylsilylcyclopentadienyl)zirconium dichloride (2l). A yellow microcrystalline powder, the yield was 1.51 g (48%). ^{1}H NMR (CDCl$_3$), δ: 0.27 (s, 9 H); 1.56—1.73 (m, 2 H); 1.94—2.10 (m, 2 H); 2.57—2.68 (m, 2 H); 2.85—2.97 (m, 2 H); 4.00 (s, 3 H); 6.03 (t, 2 H, J = 2.45 Hz); 6.41 (t, 2 H, J = 2.45 Hz); 6.54 (s, 2 H); 7.07 (td, 1 H, J = 5.01 Hz, J = 4.16 Hz, J = 1.10 Hz); 7.10 (dd, J = 7.46 Hz, J = 1.10 Hz); 7.33 (td, 1 H, J = 7.90 Hz, J = 7.46 Hz, J = 1.59 Hz); 7.58 (dd, J = 7.70 Hz, J = 1.59 Hz). ^{13}C NMR (CDCl$_3$), δ: –0.50, 21.72, 24.14, 54.72, 111.02, 111.34, 117.30, 120.77, 122.64, 123.13, 124.62, 127.15, 127.34, 128.46, 132.21, 155.27. Found (%): C, 55.40; H, 5.84. $C_{24}H_{30}Cl_2OSiZr$. Calculated (%): C, 54.94; H, 5.76.

Polymerization (general procedure). A 300-mL flask was washed with a small amount of a solution of AlMe$_3$ in toluene, then toluene (180 mL) and MAO (5 mL, 10 wt.%) were placed into this flask. The flask was equipped with a mechanical stirrer and placed in an oil bath heated to 90 °C. A metallocene catalyst (20 μmol) was dissolved in toluene (20 mL) in a separate flask. To carry out the polymerization, this solution (5 mL) was added to the mixture. Ethylene was passed through the content of the flask until saturation of the solution, the operation was repeated three times. The polymerization was carried out with stirring (500 rpm) for 30 min. Upon completion of the reaction, the mixture was cooled to ~20 °C, the content of the flask was poured into ethanol (400 mL) and this mixture was stirred for 1 h. The polymer was collected by filtration and dried in a vacuum oven for 20 h at 60 °C. A small amount of the sample was analyzed by gel-permeation chromatography.

Copolymerization of ethylene and hex-1-ene was carried out similarly to the procedure described above, except that hex-1-ene (5 mL) was added to the reaction mixture before placing it in an oil bath.

References

1. H. Sinn, W. Kaminsky, H. J. Vollmer, R. Woldt, *Angew. Chem.*, *Int. Ed. Engl.*, 1980, **19**, 390.
2. H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1143.
3. H. G. Alt, A. Köppl, *Chem. Rev.*, 2000, **100**, 1205.
4. P. C. Möhring, N. J. Coville, *J. Organomet. Chem.*, 1994, **479**, 1.
5. L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.*, 2000, **100**, 1253.
6. E. Samuel, *Bull. Soc. Chim. Fr.*, 1966, **11**, 3548.
7. W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm, W. A. Herrmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, **31**, 1347.
8. W. Kaminsky, K. Kulper, H. H. Brintzinger, F. Wild, *Angew. Chem.*, *Int. Ed. Engl.*, 1985, **24**, 507.
9. F. Piemontesi, I. Camurati, L. Resconi, D. Balboni, A. Sironi, M. Moret, R. Zeigler, N. Piccolrovazzi, *Organometallics*, 1995, **14**, 1256.
10. E. Samuel, M. D. Rausch, *J. Am. Chem. Soc.*, 1973, **95**, 6263.
11. S. M. Baldwin, J. E. Bercaw, H. H. Brintzinger, *J. Am. Chem. Soc.*, 2008, **130**, 17423.
12. R. L. Halterman, T. M. Ramsey, *J. Organomet. Chem.*, 1994, **465**, 175.
13. R. L. Halterman, T. M. Ramsey, N. A. Pailes, M. A. Khan, *J. Organomet. Chem.*, 1995, **497**, 43.
14. R. L. Halterman, K. P. C. Vollhardt, *Tetrahedron Lett.*, 1986, **27**, 1461.
15. G. Erker, A. A. H. Vanderzeijden, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 512.
16. R. L. Halterman, A. Tretyakov, *Tetrahedron*, 1995, **51**, 4371.
17. E. Polo, S. Losio, F. Fortini, P. Locatelli, M. C. Sacchi, *Macromol. Symp.*, 2004, **213**, 89.
18. A. F. Asachenko, D. S. Kononovich, A. N. Zharov, A. Razavi, A. Z. Voskoboynikov, *J. Organomet. Chem.*, 2010, **695**, 1940.
19. A. Y. Lebedev, V. V. Izmer, A. F. Asachenko, A. A. Tzarev, D. V. Uborsky, Y. A. Homutova, E. R. Shperber, J. A. M. Canich, A. Z. Voskoboynikov, *Organometallics*, 2009, **28**, 1800.
20. A. N. Ryabov, V. V. Izmer, A. A. Tzarev, D. V. Uborsky, A. F. Asachenko, M. V. Nikulin, J. A. M. Canich, A. Z. Voskoboynikov, *Organometallics*, 2009, **28**, 3614.
21. V. V. Izmer, A. Y. Lebedev, M. V. Nikulin, A. N. Ryabov, A. F. Asachenko, A. V. Lygin, D. A. Sorokin, A. Z. Voskoboynikov, *Organometallics*, 2006, **25**, 1217.
22. M. Miyashita, T. Yanami, A. Yoshikoshi, *J. Am. Chem. Soc.*, 1976, **98**, 4679.
23. R. N. Austin, T. J. Clark, T. E. Dickson, C. M. Killian, T. A. Nile, D. J. Schabacker, A. T. McPhail, *J. Organomet. Chem.*, 1995, **491**, 11.
24. K. Yu, M. W. McKittrick, C. W. Jones, *Organometallics*, 2004, **23**, 4089.

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