# Synthesis of *ansa*-zirconocenes based on 2-(phenylethynyl)-1*H*-indene. The crystal and molecular structure of the complex [μ-CH<sub>2</sub>CH<sub>2</sub>(η<sup>5</sup>-2-PhC≡CInd)<sub>2</sub>]ZrCl<sub>2</sub> (Ind is inden-1-yl)

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Alkynyl-substituted indene was first used as a ligand for the synthesis of transition metal complexes. *ansa*-Zirconocenes containing ethylene and dimethylsilylene bridges were synthesized starting from 2-(phenylethynyl)-1*H*-indene. The structure of the former compound was established by X-ray diffraction.

**Key words:** indan-2-one, 2-(phenylethynyl)-1*H*-indene, *ansa*-zirconocenes, X-ray diffraction study.

For more than 20 years, starting from the pioneering studies, 1-3 bis-indenyl ansa-complexes of Group IV elements, predominantly, zirconium(IV) complexes 1, have been considered as one of the most promising classes of catalysts for alkene polymerization.<sup>4,5</sup> Hundreds of new bis-indenyl ansa-zirconocenes have been synthesized, and the relationship between the structure of metallocenes and their catalytic properties has been established. It was found that compounds containing short bridges, such as CR<sub>2</sub>, CR<sub>2</sub>CR<sub>2</sub>, or SiR<sub>2</sub>, have high activity. Symmetric ansa-complexes exist as mixtures of two diastereomeric forms of 2, *viz.*, the *rac* form, which has  $C_2$  symmetry and catalyzes isotactic  $\alpha$ -olefin polymerization, and the meso form, which has  $C_s$  symmetry and catalyzes atactic polymerization. Hence, isolation of pure rac forms is one of problems associated with the synthesis of metallocenes as potential polymerization catalysts.



 $Z = CR_2, CR_2CR_2, SiR_2$ 

In spite of the fact that numerous indenes have been synthesized and transformed into metallocenes, some of these compounds remain poorly studied. This is particularly true for alkynylindenes. The only known representative of this group of compounds, 3-ethynyl-1H-indene (3), is unstable and its chemical properties are virtually unknown.<sup>6</sup> In addition, compound 3 contains the acidic hydrogen atom at the terminal triple bond (Scheme 1) and, consequently, it can hardly be used for the synthesis of metallocenes.



In our opinion, metallocenes based on alkynylindenes are of interest both from the point of view of the influence of the substituent on the properties of the complex and as the starting compounds for further transformations into

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more complicated, including supramolecular, structures. Due to the presence of the reactive triple bond, metallocenes can be considered as potential substrates in reactions with nucleophilic reagents and dienes. In the present study, we synthesized 2-(phenylethynyl)-1*H*-indene (4) and used it for the preparation of *ansa*-zirconocenes 5 and 6.



We chose the phenylethynyl substituent for the indene molecule because phenylacetylenes are more stable than alkylacetylenes.

## **Results and Discussion**

Synthesis of 2-(phenylethynyl)-1*H*-indene (4). We synthesized indene 4 by the reaction of PhC=CMgBr with indan-2-one followed by hydrolysis and acid-catalyzed dehydration of intermediate alcohol (Scheme 2).

#### Scheme 2



It appeared that, unlike usual Grignard reagents, which cause deprotonation of indan-2-ones,<sup>7</sup> the PhC=CMgBr reagent rather smoothly adds to the C=O bond to give, after dehydration, compound 4 in 67% yield. Unlike ethynylindene 3, compound 4 is thermally stable and can easily be purified by recrystallization.

Indenes can be used as ligands for the synthesis of complexes of Group IV elements mainly due to their ability to form rather stable alkali metal derivatives, which can be subjected to further transformations. Compound **4** reacts in diethyl ether with a solution of *n*-butyllithium to form a precipitate of its lithium derivative, which remains unchanged in appearance on storage. The lithium derivative of indene **4** was not isolated and was used *in situ* in the subsequent steps of the synthesis of bis-indenyl bridged compounds. Synthesis of bis-indenyl bridged compounds. We chose bis(2-phenylethynyl)indenyl compounds with  $CH_2CH_2$  and  $SiMe_2$  bridges as potential ligands for the synthesis of *ansa*-zirconocenes.

An attempt to synthesize the first of these compounds, viz., 2-(phenylethynyl)-3-{2-[2-(2-phenylethynyl)-1Hinden-3-yl]ethyl-1H-indene (7), according to a known procedure<sup>8</sup> (by the reaction of the lithium derivative of compound 4 with 1,2-dibromoethane in THF) failed. An analysis of the reaction mixture demonstrated that the yield of the target compound was no higher than 15%, and the mixture contained substantial amounts of 1-(2-bromoethyl)-1*H*-indene 8 and spiro derivative 9 (Scheme 3). In diethyl ether, the reaction proceeded very slowly. A satisfactory yield of compound 7 was achieved in the reaction in diethyl ether in the presence of catalytic amounts of CuNCS, which has recently found use as an efficient catalyst for the reaction of indenyllithium with chlorosilanes.<sup>9</sup> Therefore, we demonstrated that copper salts can catalyze not only silvlation but also alkylation of indenes.

Evidently, the reaction of the lithium derivative of indene **4** with dibromoethane produces a mixture of bisindenyl compounds isomeric on double bond location in the indenyl ring, which is confirmed by the appearance of signals at  $\delta 1.3-1.4$  (-CH<sub>2</sub>CH<sub>2</sub>CH<) and the presence of signals for the vinyl protons of the five-membered ring. To simplify the isolation of the product, this mixture was treated with two equivalents of *n*-butyllithium followed by hydrolysis. The resulting most stable isomer **7** was isolated by crystallization in 31% yield (see Scheme 3).

The reaction of two equivalents of the lithium derivative of indene **4** with  $SiMe_2Cl_2$  (in particular, in the presence of CuNCS as the catalyst) produced dimethyl{bis[2-(phenylethynyl)-1*H*-inden-1-yl]}silane (**10**) in satisfactory yield (>70%). However, we failed to isolate product **10** in pure form, because is does not crystallize and is insufficiently stable for preparative column chromatography.

Hence, we decided to perform the synthesis of compound **10** in two steps. First, (dimethyl)chloro[2-(phenylethynyl)-1*H*-inden-1-yl]silane (**11**) was prepared in 97% yield by the reaction of the lithium derivative of indene **4** with excess  $SiMe_2Cl_2$  in the absence of a catalyst. Then the reaction of silane **11** with the lithium derivative of indene **4** was performed in the presence of CuNCS (Scheme 4). The <sup>1</sup>H NMR spectroscopic study demonstrated that the reaction mixture contained virtually pure bis-indenyl compound **10**, which made it possible to use this mixture after minimal purification (from inorganic impurities).

Synthesis of *ansa*-zirconocenes. As a rule, *ansa*-zirconocenes are prepared by the reaction of dilithium derivatives of the corresponding bis-indenyl compounds

Scheme 3



Scheme 4



with ZrCl<sub>4</sub>. The reaction can be performed in various solvents (most commonly, in diethyl ether or THF).

The reaction of the dilithium derivative of compound 7 with ZrCl<sub>4</sub> both in diethyl ether and THF produces the target compound, *viz.*, *ansa*-zirconocene 5, in very low yield (<sup>1</sup>H NMR spectroscopic data for the reaction mixture). One of the possible ways of increasing the yield of *ansa*-zirconocenes is based on the use of distannylated derivatives of bis-indenyl compounds instead of dilithium derivatives.<sup>10</sup> We synthesized bis(triethylstannyl) derivative **12** in quantitative yield (NMR spectroscopic data for the reaction mixture) and used it for the synthesis of zirconocene **5** without additional purification. The reaction was performed in dichloromethane. The pure racemic form of **5** was isolated by recrystallization from dimethoxyethane in 68% yield (Scheme 5).



Compound **6** was synthesized according to a conventional procedure by the reaction of dilithium derivative **10** with  $ZrCl_4$  (Scheme 6). After recrystallization from dimethoxyethane, the yield of *rac*-**6** was 34%.

#### Scheme 6

**10** 
$$\xrightarrow{1) \text{BuLi/Et}_2\text{O};}{2) \text{ZrCl}_4/\text{Et}_2\text{O}}$$
 **6** (34%)

The structures of compounds **5** and **6** were established by NMR spectroscopy. The conclusion that compound **6** exists in the *rac* rather than in the *meso* form was made based on the analysis of the <sup>1</sup>H and <sup>13</sup>C NMR



Fig. 1. Molecular structure of compound 5.

spectra, which show one signal of the Me groups of the  $-SiMe_2$ - bridge. It is impossible to assign compound 5 containing the dimethylene bridge to the *rac* or *meso* form based only on the NMR spectroscopic data. Hence, we established the structure of compound 5 by X-ray diffraction.

X-ray diffraction study of compound 5. Single crystals of compound 5 were grown by diffusion crystallization from a  $CH_2Cl_2$ —diethyl ether mixture, and compound 5 was studied by X-ray diffraction, which confirmed that molecule 5 exists as the *rac* isomer (Fig. 1).

The bond lengths and bond angles in molecule **5** are given in Table 1.

In the molecule of *ansa*-complex 5, the zirconium atom is  $\eta^5$ -coordinated by the indenyl fragment and two chlorine atoms. The molecule has distortions characteris-

tic of *ansa*-metallocenes due to the presence of the short bridge between two indenyl fragments. The C(1)–C(18) and C(19)–C(20) bonds deviate from the planes of the indenyl rings, whereas no noticeable deviations of the bond lengths and bond angles from the expected values were found. The indenyl ring and the phenyl ring of the 2-PhC=C fragment are noncoplanar. The C=C bond lengths (1.186 and 1.200 Å) are typical of acetylene and substituted acetylenes. The C(sp<sup>2</sup>)–C(sp)–C(sp) bond angles (173.8–177.7°) are close to theoretical values.

The structure of the bis-indenyl *ansa*-zirconocene fragment in molecule **5** is similar to those in molecules of other ethylene-bridged bis-indenyl complexes, **13** (see Ref. 8) and, particularly, **14**.<sup>11</sup> In the latter compound, the Zr—Cl and Zr—C bond lengths and the geometry of the bridging fragment are virtually identical.

Bond	d/Å	Bond	d∕Å	Angle	ω/deg
$\overline{Zr-Cl(2)}$	2.4046(9)	C(1)-C(18)	1.494(4)	C(11)-C(10)-C(9)	177.7(3)
Zr-Cl(1)	2.4236(8)	C(18)-C(19)	1.533(4)	C(10) - C(11) - C(12)	176.4(3)
Zr-C(1)	2.485(3)	C(19)-C(20)	1.504(4)	C(1) - C(18) - C(19)	111.4(2)
Zr-C(9)	2.499(3)	C(28)-C(29)	1.424(4)	C(20) - C(19) - C(18)	111.2(2)
Zr-C(20)	2.498(3)	C(29)-C(30)	1.200(4)	C(30) - C(29) - C(28)	173.8(3)
Zr-C(28)	2.508(3)	C(30)-C(31)	1.433(4)	C(29) - C(30) - C(31)	177.6(3)
Zr-C(8)	2.541(3)	$Zr-C_{Cp(1)}$	2.542(3)	$C-C-C_{Cp(1)}$	106.2(2)-109.4(2)
Zr-C(27)	2.547(3)	$Zr-C_{Cn(2)}$	2.5612(3)	$C-C-C_{Cp(2)}$	106.6(2)-108.8(3)
Zr-C(2)	2.561(2)	$Zr-Cp(1)_{centr}$	2.235(3)	Cl(2) - Zr - Cl(1)	99.48(4)
Zr-C(21)	2.596(3)	$Zr-Cp(2)_{centr}$	2.258(3)	$Cl(1)$ -Zr- $Cp(1)_{centr}$	107.0(7)
Zr-C(7)	2.623(3)			$Cl(2) - Zr - Cp(1)_{centr}$	107.3(7)
Zr-C(26)	2.657(3)			$Cl(1)$ -Zr- $Cp(2)_{centr}$	107.3(6)
C(9) - C(10)	1.434(4)			$Cl(2)-Zr-Cp(2)_{centr}$	106.0(7)
C(10)-C(11)	1.186(4)			$Cp(1)_{centr}$ -Zr- $Cp(2)_{centr}$	126.5(2)
C(11)-C(12)	1.439(4)			Cp(1)-Cp(2)	58.6(2)

**Table 1.** Bond lengths (*d*) and bond angles ( $\omega$ ) in molecule 5

*Note.* Cp(1) and Cp(2) are the cyclopentadienyl fragments C(1)C(2)C(7)C(8)C(9) and C(20)C(21)C(26)C(27)C(28), respectively; Cp(1)<sub>centr</sub> and Cp(2)<sub>centr</sub> are the centroids of these fragments.



Therefore, the possibility of synthesizing early transition metal complexes containing the alkynyl substituent in the indenyl ring was exemplified by the synthesis of two simplest bis-indenyl *ansa*-zirconocenes with short bridges.

#### **Experimental**

All experiments were performed under argon. The lithium derivatives and zirconium complexes were synthesized in all-sealed Schlenk-type glassware. Ethereal solvents were distilled from sodium benzophenone ketyl. Dichloromethane was purified by distillation over CaH<sub>2</sub>. Indan-2-one (Acros) was used without prepurification. Phenylacetylene (Acros) was distilled under reduced pressure before use. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian VXR-400 instrument. Elemental analysis was carried out on a Carlo-Erba analyzer.

2-(Phenylethynyl)-1H-indene (4). An EtBr solution (44.7 mL, 0.6 mol) in Et<sub>2</sub>O (600 mL) was added to Mg chips (14.6 g, 0.6 mol) in Et<sub>2</sub>O (20 mL) at such a rate that steady reflux of the reaction mixture was maintained. The reaction mixture was stirred for 1 h. Then a solution of phenylacetylene (68.1 mL, 0.62 mol) in Et<sub>2</sub>O (200 mL) was added at  $\sim$ 20 °C for 30 min. The reaction mixture was stirred at ~20 °C for 1 h and then under reflux for 2 h followed by cooling to 0 °C. A solution of indan-2one (52.9 g, 0.4 mol) in diethyl ether (200 mL) was added for 10 min. The mixture was allowed to warm to ~20 °C. After 16 h, a 10% aqueous NH<sub>4</sub>Cl solution was added until the precipitate was completely dissolved. The organic phase was separated, and the aqueous phase was extracted with  $Et_2O$  (4×100 mL). The combined organic phases were dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure (10 Torr) at 80 °C; the major portion of phenylacetylene was distilled off. The residue was dissolved in benzene (200 mL). Then p-toluenesulfonic acid (0.5 g) and ethanol (2 mL) were added, and the reaction mixture was refluxed using a Dean-Stark trap until elimination of water ceased (1.5 h). The resulting red-brown solution was cooled, washed with water, a Na<sub>2</sub>CO<sub>3</sub> solution, and water to neutral pH, and dried over MgSO4. The solvent was removed under reduced pressure, and the residue was recrystallized from hexane (100 mL). The precipitate that formed was filtered off, washed with cold diethyl ether (50 mL), and dried in vacuo. The product was obtained in a yield of 58.0 g (67.4%) as a finely crystalline pale-yellow powder. Found (%): C, 94.37; H, 5.63. C<sub>17</sub>H<sub>12</sub>. Calculated (%): C, 94.41; H, 5.59. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C), δ: 3.68 (br.s, 2 H, -CH<sub>2</sub>-); 7.22 (br.s, 1 H), 7.28-7.50 (group of m, 7 H), 7.58 (m, 2 H) (H arom., -CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 20 °C), δ: 42.6 (−CH<sub>2</sub>−); 86.6, 94.0 (−C≡); 121.3, 123.4, 125.6, 126.6, 128.1, 128.2, 131.4, 137.2 (-CH=); 123.2, 127.2, 142.8, 144.0 (>C=).

2-(Phenylethynyl)-3-{2-[2-(2-phenylethynyl)-1H-inden-3yl]ethyl}-1H-indene (7). A BuLi solution (20.6 mL, 33 mmol) was added to a suspension of indene 4 (6.49 g, 30 mmol) in diethyl ether (80 mL) with cooling to -40 °C for 5 min. The slightly turbid reaction mixture was allowed to warm to ~20 °C, stirred for 2 h, and cooled to -40 °C. Then CuNCS (0.36 g, 3 mmol) was added. The reaction mixture turned slightly red. After 5 min, a solution of 1,2-dibromoethane (1.3 mL, 15 mmol) in diethyl ether (10 mL) was rapidly added, cooling being maintained. The reaction mixture was stirred with cooling for 1 h, allowed to warm to ~20 °C, stored for 16 h, and cooled to -20 °C. Then BuLi (22 mL) was added. The reaction mixture was allowed to warm to  $\sim 20$  °C and stirred for 1 h. Then a 10% aqueous NH<sub>4</sub>Cl solution (100 mL) and CH<sub>2</sub>Cl<sub>2</sub> (300 mL) were gradually added with cooling. The organic phase was separated, washed with water to neutral pH, and dried over MgSO<sub>4</sub>. The solvents were removed under reduced pressure, and the residue was recrystallized from diethyl ether (100 mL). The colorless finely crystalline powder that precipitated was filtered off and dried in vacuo. Product 7 was obtained in a yield of 2.12 g (31%). Found (%): C, 94.34; H, 5.66. C<sub>36</sub>H<sub>26</sub>. Calculated (%): C, 94.29; H, 5.71. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C), δ: 3.18 and 3.56 (both s, 4 H each, -CH<sub>2</sub>-); 7.18-7.35 (group of m, 14 H, H arom.); 7.40 (d, 2 H, H arom.,  ${}^{3}J = 7.8$  Hz); 7.56 (d, 2 H, H arom.,  ${}^{3}J =$ 7.6 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 20 °C), δ: 26.1, 41.5 (-CH<sub>2</sub>-); 86.2, 96.1 (-C=); 119.4, 123.6, 126.4, 127.8, 128.1, 131.3, 125.6 (-CH=); 123.4, 123.6, 142.9, 144.4, 149.5 (>C=).

The reaction in THF afforded a complex mixture of products. The <sup>1</sup>H NMR spectrum of the mixture shows signals of compound **7** and the isomeric bis-indenyl compounds, as well as characteristic signals of compounds **8** ( $\delta$  2.57 and 3.44, both m, CH<sub>2</sub>CH<sub>2</sub>Br) and **9** ( $\delta$  1.72 and 1.93, both m, CH<sub>2</sub>CH<sub>2</sub>). After distillation at 140–150 °C (0.5 Torr), the fraction containing virtually pure compound **9** and an insignificant impurity of indene **4** was distilled off.

<u>Compound 9</u>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C),  $\delta$ : 1.72 and 1.93 (both m, 2 H each,  $-CH_2$ — of the cyclopropane ring); 7.27 (br.s, 1 H, =CH— of the five-membered ring); 7.07–7.63 (group of m, 9 H, -CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 20 °C),  $\delta$ : 15.5 ( $-CH_2$ —); 34.6 (>C<); 83.3, 95.8 (-C=); 117.6, 121.8, 125.1, 125.8, 128.2, 131.3, 131.4, 132.7 (-CH=); 123.0, 132.4, 137.2, 147.6 (>C=).

(Dimethyl)chloro[2-(phenylethynyl)-1H-inden-1-yl]silane (11). A BuLi solution (15 mL, 24 mmol) was added to a suspension of indene 4 (4.32 g, 20 mmol) in diethyl ether (70 mL) with cooling to -40 °C for 5 min. The slightly turbid reaction mixture was allowed to warm to ~20 °C and stirred for 2 h. Then the reaction mixture was cooled to -40 °C, and SiMe<sub>2</sub>Cl<sub>2</sub> (3.6 mL, 30 mmol) was added. The reaction mixture was stirred with cooling for 1 h, allowed to warm to ~20 °C, stored for 16 h, and filtered. The filtrate was concentrated under reduced pressure. The residue (a pale-yellow oil) was dried in vacuo. The yield of product 11 was 5.98 g (97%). Found (%): C, 73.99; H, 5.65. C<sub>19</sub>H<sub>17</sub>ClSi. Calculated (%): C, 73.88; H, 5.55. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C), δ: 0.20 and 0.82 (both s, 3 H each, Me); 4.00 (s, 1 H, -CH<); 7.37-7.47 (group of m, 6 H), 7.57 (br.d, 1 H,  ${}^{3}J = 7.2$  Hz), 7.64 (m, 2 H), 7.78 (br.d, 1 H,  ${}^{3}J = 7.2$  Hz) (H arom., -CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 20 °C), δ: 1.67, 1.87 (Me); 49.8 (-CH<); 87.0, 95.4 (-C=); 121.4, 123.7, 125.3, 126.1, 128.2, 128.3, 131.1, 136.6 (-CH=); 123.1, 126.6, 143.0, 143.3 (>C=).

Dimethyl{bis[2-(phenylethynyl)-1*H*-inden-1-yl]}silane (10). A BuLi solution (12.5 mL, 20 mmol) was added to a suspension of indene 4 (4.11 g, 19 mmol) in diethyl ether (80 mL) with cooling to -40 °C for 5 min. The reaction mixture was allowed to warm to ~20 °C, stirred for 2 h, and cooled to -40 °C. Then CuNCS (0.24 g, 2 mmol) was added. After 5 min, a solution of silane 11 (5.87 g, 19 mmol) in diethyl ether (20 mL) was added for 10 min, cooling being maintained. The reaction mixture was stirred with cooling for 1 h. Then the mixture was allowed to warm to ~20 °C, stirred for 16 h, and cooled to 0 °C. A 10% aqueous NH<sub>4</sub>Cl solution (20 mL) was added. The organic phase was separated, washed with water to neutral pH, and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure, and the residue was dried in vacuo. The reaction product (9.3 g, a dark-yellow viscous oil) contained a mixture of rac and meso diastereomers and was virtually free of impurities of indene 4. The product was used without additional purification. Found (%): C, 88.65; H, 5.88. C<sub>36</sub>H<sub>28</sub>Si. Calculated (%): C, 88.48; H, 5.78. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C), δ: -0.29, -0.21, and -0.08 (all s, 6 H, Me); 4.52 and 4.76 (both s, 2 H, -CH<); 7.20–7.72 (group of m, 20 H, H arom., –CH=).

 $\mu$ -{Bis[ $\eta^{5}$ -2-(phenylethynyl)-1*H*-inden-1-yl]-1,2-ethanediyl}dichlorozirconium(IV) (5). A BuLi solution (2 mL, 3.2 mmol) was added with stirring and cooling to -20 °C to a solution of compound 7 (0.50 G, 1.09 mmol) in diethyl ether (40 mL), which gave rise to a lemon-yellow dilithium derivative. The reaction mixture was allowed to warm to ~20 °C, stirred for 1.5 h, and cooled to -40 °C. Then Et<sub>3</sub>SnCl (0.54 mL, a minimal excess with respect to BuLi) was added. The resulting palevellow solution of compound 12 was separated from LiCl by decantation, the solvent was removed, and a small amount was taken for NMR spectroscopy. Then CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added, the mixture was cooled to -20 °C, and ZrCl<sub>4</sub> (0.254 g, 1.1 mmol) was added with vigorous stirring. The reaction mixture was stirred for 1 h without cooling and kept for ~14 h. The solution was separated by decantation, and the precipitate was washed with small portions of CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed (the residue fully crystallized out), and diethyl ether (20 mL) was added. The precipitate was washed with diethyl ether (4×10 mL), recrystallized from dimethoxyethane, and dried in vacuo. The yield of the rac form of 5 was 210 mg (68%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), δ: 4.10 (AA'BB' system, 4 H, -CH<sub>2</sub>CH<sub>2</sub>-); 6.73 (s, 2 H, H arom.); 6.90 (dd, 2 H, H arom.,  ${}^{3}J = 9.2$  Hz,  ${}^{3}J = 7.2$  Hz); 7.31 (dd, 2 H, H arom.,  ${}^{3}J = 8.4$  Hz,  ${}^{3}J = 7.2$  Hz); 7.82 (d, 2 H, H arom.,  ${}^{3}J = 9.2$  Hz); 7.42 (d, 2 H, H arom.,  ${}^{3}J = 8.4$  Hz); 7.47 (m, 6 H, H arom.); 7.61 (m, 4 H, H arom.). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C),  $\delta$ : 28.9 (-CH<sub>2</sub>-); 83.6, 97.6 (-C=); 112.4, 122.7, 123.0, 130.2 (>C=); 114.4, 124.0, 125.3, 126.2, 127.7, 129.0, 129.5, 131.9 (-CH=).

The <sup>1</sup>H NMR spectrum of intermediate compound **12** (benzene-d<sub>6</sub>, 20 °C,  $\delta$ ): 0.97 (m, 12 H, Sn–CH<sub>2</sub>—); 1.18 (m, 18 H, Sn–CH<sub>2</sub>C<u>H<sub>3</sub></u>); 3.62–3.76 (group of m, –CH<sub>2</sub>CH<sub>2</sub>—); 4.32 and 4.33 (both s, 2 H, >CH–); 7.10–8.10 (group of m, 18 H, H arom.). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, 20 °C),  $\delta$ : 1.8 (Sn–C); 8.4 (–CH<sub>2</sub>CH<sub>2</sub>—); 10.0 (>CH–); 11.1 (Sn–CH<sub>2</sub>C<u>H<sub>3</sub></u>); 28.1, 28.2, 29.6, 30.2 (>C= of the five-membered ring); 87.7, 87.8, 96.6, 96.7 (–C=); 120.3, 120.4, 122.0, 122.1, 124.6, 124.8, 128.6, 128.7, 131.5, 131.6 (–CH=); 111.8, 144.2, 144.3, 146.8, 146.9 (>C=).

 $\mu$ -{Bis[ $\eta^5$ -2-(phenylethynyl)-1*H*-inden-1-yl]dimethylsilanediyl}dichlorozirconium(iv) (6). A 1.6 *M* BuLi solution (25 mL, Table 2. Principal crystallographic data for compound 5

Parameter	Characteristic
Molecular formula	C <sub>36</sub> H <sub>24</sub> Cl <sub>2</sub> Zr
Molecular weight	618.67
Crystal dimension/mm	0.2×0.2×0.2
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	16.814(3)
b/Å	17.702(4)
c/Å	9.258(2)
α/deg	90
β/deg	94.42(3)
γ/deg	90
V/Å <sup>3</sup>	3275.3(11)
Z	8
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.291
$\mu/\text{mm}^{-1}$	0.075
Number of reflections	4444
Number of independent reflections	4023
R <sub>int</sub>	0.0217
Extinction coefficient	0.0018(4)
$R_1$ , $wR_2$ based on reflections with $F > 2\sigma(F)$	0.0257, 0.0723
$R_1$ , $wR_2$ based on all reflections	0.0622, 0.0887

40 mmol) was added to a solution of compound **10** (9.4 g, 19.23 mmol) in diethyl ether (80 mL) with cooling to -20 °C. The mixture was allowed to warm to  $\sim 20$  °C, stirred for 16 h, and cooled to -40 °C. Then ZrCl<sub>4</sub> (4.48 g, 19.23 mmol) was added, after which a yellow-orange precipitate was immediately formed. The reaction mixture was allowed to warm to  $\sim 20$  °C and stirred for 16 h. The precipitate was separated by filtration, recrystallized from dimethoxyethane, and dried *in vacuo*. The yield of the *rac* form of **6** was 2.12 g (34%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C),  $\delta$ : 1.52 (s, 6 H, Me); 6.70 (dd, 2 H, <sup>3</sup>J = 8.9 Hz, <sup>3</sup>J = 6.7 Hz), 7.09 (s, 2 H), 7.35 (dd, 2 H, <sup>3</sup>J = 8.9 Hz, <sup>3</sup>J = 6.7 Hz), 7.45 and 7.52 (both m, 6 H each), 7.76 (d, 2 H, <sup>3</sup>J = 8.9 Hz) (all H arom.). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C),  $\delta$ : 0.75 (Me); 86.3, 88.5 (-C=); 96.8, 115.6, 122.9, 127.0, 133.6 (>C=); 122.7, 125.4, 126.2, 127.7, 129.0, 128.5, 129.5, 131.6 (-CH=).

X-ray diffraction study of compound 5. The unit cell parameters and the X-ray diffraction set were measured on an automated four-circle KM-4 diffractometer (KUMA DIFFRACTION) at 293.0(2) K (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\omega$ -scanning technique). The structure was solved by direct methods and refined by the full-matrix least-squares method against  $F^2$ . The hydrogen atoms were located from a difference Fourier map and refined isotropically. The bond lengths and bond angles in molecule 5 are given in Table 1. The X-ray data collection and refinement statistics are listed in Table 2.

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