

# Synthesis and photoinduced isomerization of *ansa*- $\{\eta^5, \eta^{5'}-[1,1'-(1\text{-silacyclopent-3-ene-1,1-diyl})\text{bis(indenyl)}]\}$ -dichlorozirconium. The crystal structure of its *meso* form

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*ansa*- $\{\eta^5, \eta^{5'}-[1,1'-(1\text{-Silacyclopent-3-ene-1,1-diyl})\text{bis(indenyl)}]\}$ dichlorozirconium (**1a,b**) was synthesized. The crystal structure of *meso*- $\{(1,4\text{-CH}_2\text{CH=CHCH}_2\text{)Si(C}_6\text{H}_5\text{)}_2\text{ZrCl}_2\}$  (**1b**) was established by X-ray diffraction analysis. Photoinduced interconversion of the racemic (**1a**) and *meso* forms was studied under various conditions. The photostationary state (*rac* : *meso* = 55 : 45) was established rapidly when solutions of *ansa*-zirconocene were irradiated with visible light.

**Key words:** *ansa*-zirconocenes, crystal structure, photoinduced isomerization.

It is well known (see, for example, the review 1) that chiral bridged metallocenes are widely used as homogeneous catalysts in polymerization and copolymerization of various  $\alpha$ -olefins, in particular, in industrial propylene polymerization. One way of improving the efficiency of these processes is to immobilize the catalyst on the surface of a solid-phase carrier and to perform the reaction under virtually heterogeneous conditions. In this connection, *ansa*-metallocenes whose bridging fragments contain the double bond, which can undergo further functionalization followed by "attachment" to the corresponding solid phase, show promise.

Besides, it was established that individual isomers (the racemate and the *meso* form) of chiral metallocenes can undergo interconversions upon photoexcitation. These photoinduced interconversions of stereoisomers were reported for a number of titanium complexes<sup>2–5</sup> and were recently studied for some zirconocenes.<sup>6–8</sup> The racemic form of the catalyst is the active principle in the processes of stereospecific polymerization. Therefore, studies of the photochemical behavior of chiral metallocenes are of obvious theoretical and practical interest.

In this work, we synthesized a mixture of the racemic (**1a**) and *meso* forms of *ansa*- $\{\eta^5, \eta^{5'}-[1,1'-(1\text{-silacyclopent-3-ene-1,1-diyl})\text{bis(indenyl)}]\}$ dichlorozirconium (**1b**) containing the unsaturated bridging fragment and studied photoinduced interconversion of the racemic and *meso* forms under various conditions. The crys-

tal structure of *meso* form **1b** was established by X-ray diffraction analysis.

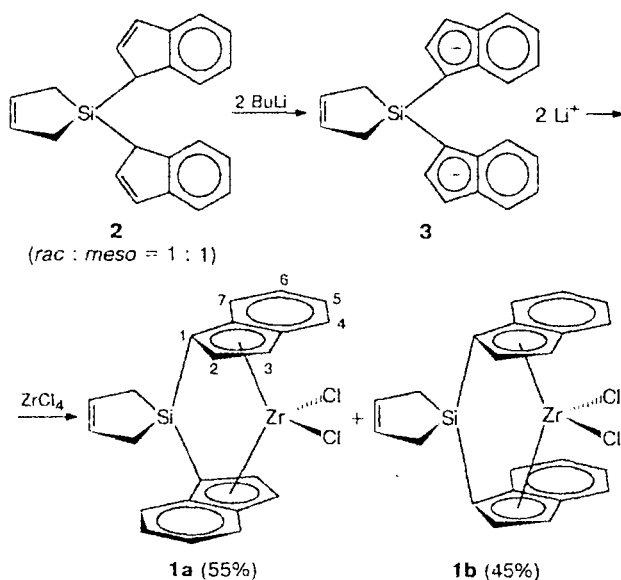
## Results and Discussion

### Synthesis of *ansa*-zirconocene **1a,b**

The synthesis of *ansa* complex **1a,b** is shown in Scheme 1. The reaction of 1,1-dichloro-1-silacyclopentene-3 with indenyllithium in Et<sub>2</sub>O proceeded smoothly under mild conditions to give 1,1'-(1-silacyclopentene-3-diyl)bis(indene) (**2**) (*rac* : *meso* = 1 : 1) in quantitative yield. Deprotonation of **2** with two equivalents of *n*-butyllithium in ether afforded the dilithium salt of the dianion (**3**), which was isolated in the crystalline form as an adduct with one Et<sub>2</sub>O molecule. Salt **3** was characterized by <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H NMR spectroscopy. The reaction of equimolar amounts of etherate **3** and ZrCl<sub>4</sub> in toluene gave *ansa*-zirconocene **1a,b** as a mixture of diastereomers **1a** and **1b** (*rac* : *meso* = 55 : 45) in good yield. Subsequent fractional crystallization from dichloromethane resulted in isolation of *meso* form **1b** in the pure form in 25% yield. The crystal structure of **1b** was established by X-ray diffraction analysis. The poorer solubility of the *meso* form compared to that of the racemate is rather unexpected because the *meso* forms of the dimethylsilyl derivative Me<sub>2</sub>Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> <sup>9</sup> (**4**) and of the saturated analog of complex **1**, [(CH<sub>2</sub>)<sub>4</sub>Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub>] <sup>10</sup> (**5**) are more soluble than the corresponding racemates. Apparently, this is associated with the peculiarities of the crystal packing of the complex. Unfortunately, we failed to

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Scheme 1



isolate pure racemate **1a** in the crystalline form because of its higher solubility as well as because of the fact that

photoinduced interconversion of **1a** and **1b** proceeded readily (see below). The best ratio of **1a** : **1b** isomers, which was attained in the mother liquor, was 2 : 1.

The parameters of the  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra of isomers **1a** and **1b** in the region of the signals of the indenyl fragments are virtually identical to those obtained previously<sup>10</sup> for the silacyclopentane derivative **5**. In the  $^1\text{H}$  NMR spectrum of racemate **1a**, the protons of the bridging  $\text{CH}_2$  fragment give an AB system with the geminal spin-spin coupling constant  $^2J_{\text{H-H}} = 17$  Hz (i.e., the protons of each  $\text{CH}_2$  group are nonequivalent). The  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum has one signal of the  $\text{CH}_2$  group ( $\delta$  16.99), which corresponds to the molecular symmetry  $C_2$ . In the case of *meso* form **1b**, the  $\text{CH}_2$  groups are nonequivalent and give two signals each in the  $^1\text{H}$  NMR ( $\delta$  2.29 and 2.64) and  $^{13}\text{C}\{-^1\text{H}\}$  NMR ( $\delta$  16.45 and 16.86) spectra, which is indicative of the presence of a symmetry plane in the molecule (the point group  $C_s$ ).

#### Crystal structure of *meso* form **1b**

The structure of complex **1b** was confirmed by X-ray diffraction analysis (Fig. 1, Tables 1–3). Molecule **1b** is a skewed metallosandwich with nearly planar indenyl

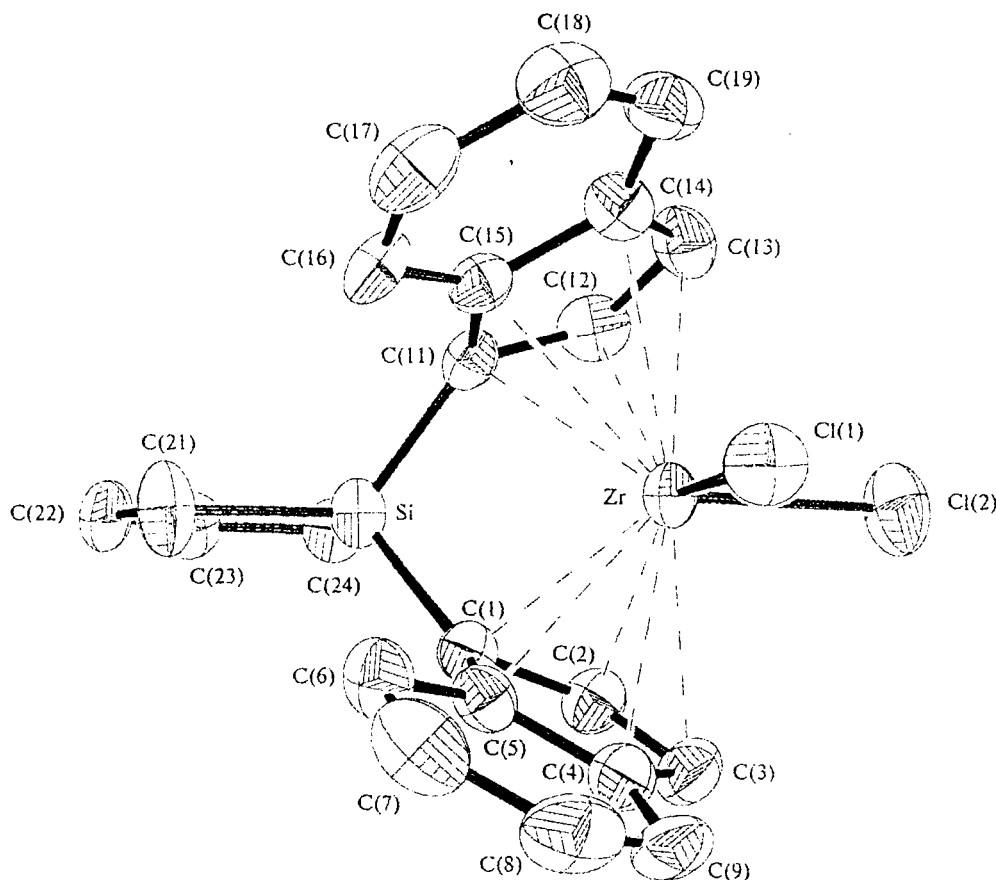


Fig. 1. Molecular structure of complex **1b**.

**Table 1.** Coordinates of nonhydrogen atoms ( $\times 10^4/\text{\AA}$ ) and their isotropic equivalent thermal parameters ( $\times 10^3/\text{\AA}^2$ ) for complex **1b**

Atom	x	y	z	$U_{eq}$
Zr	616(1)	1723(1)	1989(1)	29(1)
Si	3326(2)	2661(1)	-941(1)	34(1)
Cl(1)	-201(2)	2283(1)	4328(1)	44(1)
Cl(2)	-1213(2)	170(1)	2327(1)	57(1)
C(1)	1280(6)	3328(3)	74(3)	33(1)
C(2)	-30(6)	2751(4)	147(4)	39(1)
C(3)	-1388(6)	3146(4)	1326(4)	44(1)
C(4)	-979(6)	4042(4)	2015(4)	39(1)
C(5)	620(6)	4126(3)	1283(4)	34(1)
C(6)	1375(6)	4950(4)	1767(4)	43(1)
C(7)	453(8)	5635(4)	2928(5)	55(2)
C(8)	-1145(8)	5544(4)	3652(5)	55(2)
C(9)	-1883(6)	4766(4)	3224(4)	48(1)
C(11)	3378(5)	1339(3)	305(3)	31(1)
C(12)	2720(6)	157(4)	455(4)	42(1)
C(13)	2404(6)	-396(3)	1752(4)	43(1)
C(14)	2913(6)	393(3)	2450(4)	39(1)
C(15)	3508(5)	1478(3)	1567(3)	32(1)
C(16)	4115(6)	2428(4)	2015(4)	39(1)
C(17)	4137(6)	2269(5)	3261(4)	51(1)
C(18)	3566(6)	1195(5)	4121(4)	53(1)
C(19)	2956(6)	274(4)	3752(4)	46(1)
C(21)	4819(7)	3830(4)	-1465(4)	54(2)
C(22)	5660(6)	3647(4)	-2994(4)	49(1)
C(23)	5179(6)	2830(4)	-3567(4)	46(1)
C(24)	3828(6)	2111(4)	-2697(4)	39(1)

**Table 2.** Bond lengths ( $d$ ) in complex **1b**

Bond	$d/\text{\AA}$	Bond	$d/\text{\AA}$
Zr—Cl(1)	2.397(2)	Zr—Cl(2)	2.435(2)
Zr—C(1)	2.475(4)	Zr—C(11)	2.474(4)
Zr—C(2)	2.467(4)	Zr—C(12)	2.463(4)
Zr—C(3)	2.578(5)	Zr—C(13)	2.552(4)
Zr—C(4)	2.664(4)	Zr—C(14)	2.648(5)
Zr—C(5)	2.556(4)	Zr—C(15)	2.582(5)
Si—C(1)	1.845(5)	Si—C(11)	1.865(4)
Si—C(21)	1.873(5)	Si—C(24)	1.863(4)
C(1)—C(2)	1.432(6)	C(11)—C(12)	1.423(6)
C(1)—C(5)	1.450(5)	C(11)—C(15)	1.445(5)
C(2)—C(3)	1.408(7)	C(12)—C(13)	1.399(5)
C(3)—C(4)	1.426(6)	C(13)—C(14)	1.414(6)
C(4)—C(5)	1.398(6)	C(14)—C(19)	1.425(5)
C(4)—C(9)	1.420(6)	C(14)—C(15)	1.433(5)
C(5)—C(6)	1.447(6)	C(15)—C(16)	1.421(6)
C(6)—C(7)	1.366(6)	C(16)—C(17)	1.357(6)
C(7)—C(8)	1.398(7)	C(17)—C(18)	1.408(7)
C(8)—C(9)	1.364(7)	C(18)—C(19)	1.352(6)
C(21)—C(22)	1.510(6)	C(23)—C(24)	1.491(7)
C(22)—C(23)	1.322(6)		
Zr—Cp(1) <sup>a</sup>	2.243	Zr—Cp(2) <sup>a</sup>	2.238
Zr—PL(1) <sup>b</sup>	2.223	Zr—PL(2) <sup>b</sup>	2.229

<sup>a</sup> Cp is the center of the cyclopentadienyl ring.<sup>b</sup> PL is the plane of the cyclopentadienyl ring.**Table 3.** Selected bond angles ( $\omega$ ) in complex **1b**

Angle	$\omega/\text{deg}$
Cl(1)—Zr—Cl(2)	99.23(6)
C(1)—Si—C(24)	116.5(2)
C(1)—Si—C(11)	95.9(2)
C(24)—Si—C(11)	115.2(2)
C(1)—Si—C(21)	116.5(2)
C(24)—Si—C(21)	96.6(2)
C(11)—Si—C(21)	117.7(2)
C(22)—C(21)—Si	102.1(3)
C(23)—C(24)—Si	102.7(3)
C(23)—C(22)—C(21)	118.9(4)
C(22)—C(23)—C(24)	119.7(4)
Cp(1)—Zr—Cp(2)*	127.7
PL(1)—PL(2)*	118.9
Si—C(1)—Cp(1)	162.8
Si—C(11)—Cp(2)	162.3

\* See notes in Table 2.

ligands (the mean deviations of the carbon atoms from the C(1)—C(9) and C(11)—C(19) planes are 0.012 and 0.023 Å, respectively). The bridging silacyclopentene group is also virtually planar (the maximum deviation of the Si atom from the plane through the five atoms is 0.019 Å). The Zr—C bond distances vary in a rather wide range from 2.463(4) Å (for the C(12) atom) to 2.664(4) Å (for the C(4) atom). The substantial decrease in the Zr—C(2) distance compared to the Zr—C(4) distance is rather typical of bisindenyl zirconocenes and reflects the noticeable tendency of **1b** to  $\eta^3$ -coordination with the indenyl ligand. Thus, analysis of the data available in the Cambridge Structural Database (CSD, November 1997<sup>11</sup>) demonstrated that for 29 structures of bisindenylzirconocene dichlorides, the average Zr—C(2) distance is 2.525 Å, whereas the Zr—C(4) distance is 2.587 Å.

The principal structural parameters of complex **1b** and two related compounds,  $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)_2\text{ZrCl}_2]$  (**4**) and  $[(\text{CH}_2)_4\text{Si}(\text{C}_9\text{H}_6)_2\text{ZrCl}_2]$  (**5**) (calculations from the CSD data), are given in Table 4. On the whole, both for the *rac* and *meso* forms of these compounds, the parameters that characterize the metallocene fragment (the Cl—Zr—Cl and Cp(center)—Zr—Cp(center) angles and the Cp(center)—Zr distances) change only slightly. The same is true for the characteristics of the strain of the bridging dialkylsilyl group (the  $\text{C}_{\text{ind}}\text{—Si—C}_{\text{ind}}$  and Cp(center)— $\text{C}_{\text{ind}}\text{—Si}$  angles). However, it should be noted that in the *meso* complexes, unlike the *rac* forms, substantial differences are observed in the Zr—Cl bond lengths. The distances to the chlorine atom shielded by both phenyl rings are 0.046 and 0.038 Å shorter than the distances to the nonscreened atom.

It should be also noted that although crystals of **1b** and of *meso* form **5** belong to the same space group and

**Table 4.** Comparison of the structural parameters of complexes **1b**, **4**, and **5**

Complex, isomer	Zr—Cl	$\delta(\text{Zr—Cl})^a$	Cl—Zr—Cl	$\text{C}_R\text{—Si}^b$	$\text{C}_R\text{—Si—C}_R$	$\text{C}_{\text{ind}}\text{—Si}^c$	$\text{C}_{\text{ind}}\text{—Si—C}_{\text{ind}}$	Zr—Cp <sup>d</sup>	Cp—Zr—Cp	Cp—C <sub>ind</sub> —Si
	Å		/deg	/Å	/deg	/Å	/deg	/Å		deg
<b>1b</b>	2.435 2.397	0.038	99.23	1.873 1.863	96.6	1.865 1.845	95.9	2.243 2.238	127.7	162.8 162.3
<b>4</b> , <i>rac</i>	2.431	0	98.76	1.849	111.3	1.871	94.6	2.241	127.8	163.5
<b>5</b> , <i>rac</i>	2.432 2.426	0.006	98.25	1.878 1.875	96.5	1.866 1.855	95.2	2.261 2.247	127.6	164.3 163.0
<b>5</b> , <i>meso</i>	2.451 2.405	0.046	97.27	1.877 1.877	96.8	1.872 1.871	95.4	2.254 2.246	127.7	163.7 162.2

<sup>a</sup>  $\delta(\text{Zr—Cl})$  is the difference between the Zr—Cl(1) and Zr—Cl(2) distances.

<sup>b</sup>  $\text{C}_R$  is the carbon atom of the alkyl substituent at the bridging Si atom.

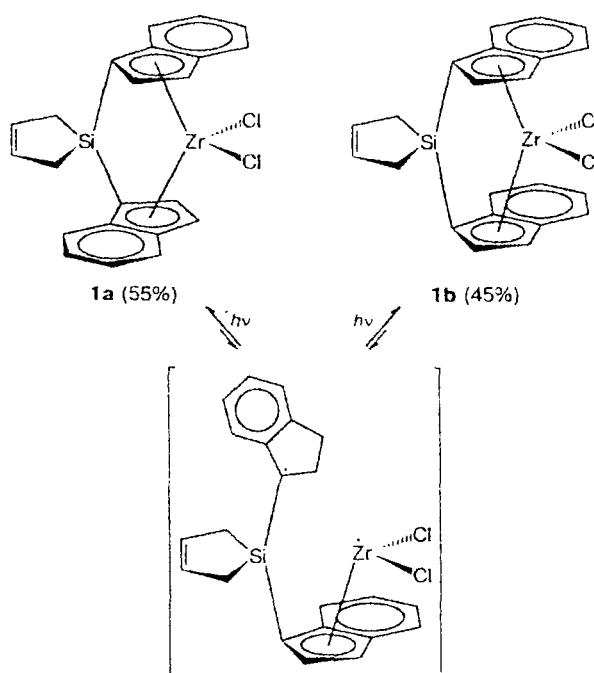
<sup>c</sup>  $\text{C}_{\text{ind}}$  is the carbon atom of the indenyl ligand bonded to the bridging Si atom. <sup>d</sup> Cp is the center of the cyclopentadienyl ring.

their unit cell parameters and the molecular geometries are similar, these compounds are not isostructural.

#### Photoinduced isomerization of isomers **1a** and **1b**

With the aim of revealing the photochemical behavior of complexes **1a,b** in solutions under irradiation both with UV and visible light, we carried out a series of experiments in various solutions. Samples were irradiated directly in NMR tubes. Ratios of the isomers were determined from the  $^1\text{H}$  NMR spectra. Solutions of the pure *meso* form and of a mixture of isomers enriched with the racemate (2 : 1) were used as the initial samples. To examine the possibility of thermal isomerization, samples were preliminarily heated in the dark at 80–90 °C for 1 h. No changes in the isomeric composition of **1a** and **1b** were observed.

We found that when solutions of **1a** and **1b** in  $\text{CD}_2\text{Cl}_2$ ,  $\text{THF-d}_8$ , and  $\text{C}_6\text{D}_6$  were irradiated with UV light (high-pressure mercury lamp, 120 W), the photostationary state (*rac* : *meso* = 55 : 45) (Scheme 2), which is independent of the solvent, was reached in a few minutes. Further irradiation of the samples for 1 h did not lead either to a change in the ratio of the isomers in the solution or to their photochemical destruction. This destruction was observed when a solution of 2,3-butenylene-1,1'-bis(tetrahydroindenyl)dichlorozirconium in THF was irradiated with UV light.<sup>6</sup> We also found that in all three solvents the photostationary state was attained within 20 min after irradiation with the use of an ordinary incandescent lamp (150 W) even when solutions of the pure *meso* form **1b** were used as the starting samples. It should be noted that even storage of solutions of **1b** in  $\text{CH}_2\text{Cl}_2$  or THF (but not in benzene) in the scattered daylight over a rather prolonged period (1–2 weeks) resulted in photoisomerization to give a virtually stationary ratio of the isomers.

**Scheme 2**

An analogous photoinduced interconversion (including that induced by visible light) was observed previously<sup>7</sup> in the case of a number of indenyl zirconocenes, in particular, in the case of dimethylsilyl derivative **4**. However, the rate of the last-mentioned interconversion was substantially lower. The photostationary ratio of the isomers found in the last-mentioned case (*rac* : *meso* = 1.2 : 1) virtually coincides with that determined by us for **1a** and **1b** (55 : 45). It should be also noted that the data on photoisomerization of silacyclopentane derivative **5** are unavailable.<sup>10</sup>

Therefore, our results demonstrate that in some cases, photoinduced interconversion of stereoisomers of chiral *ansa*-metallocenes can proceed very readily even under irradiation with visible light. This fact should be taken into account both in the synthesis of complexes and in the catalytic reactions with their participation.

### Experimental

All operations associated with the synthesis, including preparation of samples for NMR spectral studies, were carried out in all-sealed evacuated vessels of the Schlenk tube type. The solvents were dried according to conventional procedures, degassed, and introduced into the reaction volumes by recondensation using a vacuum line. Commercially available  $\text{ZrCl}_4$  (Merck) was used. 1,1-Dichloro-1-silacyclopentene-3 was purified by boiling with an aluminum powder followed by double recondensation using a vacuum line. Indenyllithium was prepared by deprotonation of indene with butyllithium and purified by recrystallization from  $\text{Et}_2\text{O}$ . The  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra were recorded on a Varian VXR-400 spectrometer (at 400 and 100 MHz, respectively) at 30 °C.

Solutions of the complex were irradiated with UV light (DRK-120 high-pressure mercury lamp, 120 W) and with visible light (incandescent lamp, 150 W) using NMR tubes placed at a distance of 15 cm from the light source; the samples were cooled with an air stream (the temperature of the samples was 40–50 °C).

**Synthesis of 1,1'-(1-silacyclopent-3-en-1,1-diyl)bis(indene) (2)** ( $(1,4\text{-CH}_2\text{CH=CHCH}_2)\text{Si}(\text{C}_9\text{H}_7)_2$ , *rac* : *meso* = 1 : 1). A solution of indenyllithium (4.58 g, 37.51 mmol) in  $\text{Et}_2\text{O}$  (20 mL) was added with intense stirring and cooling (from –30 to –40 °C) to a solution of 1,1-dichloro-1-silacyclopentene-3 (2.86 g, 18.68 mmol) in  $\text{Et}_2\text{O}$  (30 mL) for 30 min. The mixture was allowed to warm to –20 °C and kept for 12 h. The solution was filtered off from a precipitate of lithium chloride. The solvent was distilled off. Pentane (50 mL) was added. The mixture was filtered, and the solvent was distilled off. The residual pale-yellow oil was dried under high vacuum. The target compound was obtained in virtually quantitative yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 1.00 (br.s, 2 H,  $\text{CH}_2\text{Si}$ , *meso*); 1.12 (AB system, 2 H,  $\text{CH}_2\text{Si}$ , *rac*,  $^2J_{\text{H-H}} = 17.5$  Hz); 1.20 (AB system, 2 H,  $\text{CH}_2\text{Si}$ , *rac*,  $^2J_{\text{H-H}} = 17.5$  Hz); 1.38 (br.s, 2 H,  $\text{CH}_2\text{Si}$ , *meso*); 3.97 (s, 2 H, H-1); 4.00 (s, 2 H, H-1); 5.77 (m, 1 H,  $=\text{CH}-\text{CH}_2\text{Si}$ , *meso*); 5.87 (s, 2 H,  $=\text{CH}-\text{CH}_2\text{Si}$ , *rac*); 5.90 (m, 1 H,  $=\text{CH}-\text{CH}_2\text{Si}$ , *meso*); 6.64 (dd, 2 H, H-2); 6.75 (dd, 2 H, H-2); 7.17 (m, 4 H, H-3); 7.41 (t, 4 H); 7.50 (m, 4 H); 7.70 (m, 8 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 12.28 ( $\text{CH}_2\text{Si}$ , *meso*); 12.89 ( $\text{CH}_2\text{Si}$ , *rac*); 13.26 ( $\text{CH}_2\text{Si}$ , *meso*); 42.96, 43.05 (C-1, *rac*, *meso*); 121.16 (CH); 121.23 (CH); 122.89 (CH); 122.99 (CH); 124.05 (CH); 124.09 (CH); 125.30 (CH); 129.81 (CH); 129.87 (CH); 134.47 (CH); 130.33 ( $=\text{CH}-\text{CH}_2\text{Si}$ , *meso*); 130.45 ( $=\text{CH}-\text{CH}_2\text{Si}$ , *meso*, *rac*); 144.00 (two C); 144.21 (C); 144.27 (C).

**Synthesis of [1,1'-(1-silacyclopent-3-en-1,1-diyl)bis(indenyl)]dilithium (3)** (1 : 1 adduct with  $\text{Et}_2\text{O}$  ( $1,4\text{-CH}_2\text{CH=CHCH}_2\text{Si}(\text{C}_9\text{H}_6)_2\text{Li}_2 \cdot \text{Et}_2\text{O}$ )). A 2.16 M solution of *n*-butyllithium (15.2 mL) in hexane (16.45 mmol) was

**Table 5.** Crystallographic characteristics and details of data collection and of the structure solution and refinement of complex 1b

Molecular formula	$\text{Zr}_1\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{Si}_1$	Number of measured reflections	2695
Molecular weight	472.57	Number of independent reflections	2377 ( $R_{\text{int}} = 0.0301$ )
System	Triclinic	Number of reflections with $I > 2\sigma(I)$	2199
Space group	$P\bar{1}$	Procedure for the structure solution	Direct (SHELX-86) <sup>12</sup>
$a/\text{\AA}$	9.573(3)	Refinement procedure	Full-matrix least-squares procedure based on $F^2$ with anisotropic thermal parameters for nonhydrogen atoms (SHELXL-93) <sup>13</sup>
$b/\text{\AA}$	10.385(6)	Refinement of hydrogen atoms	All H atoms were placed in calculated positions ( $d(\text{C-H}) = 0.96$ \AA) and refined using the riding model
$c/\text{\AA}$	10.837(6)	Number of refinable parameters	236
$\alpha/\text{deg}$	85.78(5)	$R$ -factors with $I > 2\sigma(I)$	$R_1 = 0.0281$ , $wR_2 = 0.0812$
$\beta/\text{deg}$	64.33(4)	$R$ -factors (all reflections)	$R_1 = 0.0517$ , $wR_2 = 0.1532$
$\gamma/\text{deg}$	82.15(4)	Weighting scheme, $w^{-1}$	$\sigma^2(F_o^2) + (0.0423P)^2 + 1.073P$ , where $P = (F_o^2 + F_c^2)/3$
$V/\text{\AA}^3$	961.8(8)	Goodness of fit based on $F^2$	1.155
$Z$	2	Extinction coefficient	0.004(2)
Calculated density/ $\text{g cm}^{-3}$	1.632	Residual electron density, min/max ( $\text{e} \cdot \text{\AA}^{-3}$ )	–0.602/0.432
$F(000)$	476		
Absorption coefficient/ $\text{mm}^{-1}$	0.915		
Crystal dimensions	$0.6 \times 0.3 \times 0.2$		
Diffractionmeter	Enraf-Nonius CAD4		
Temperature/K	293(2)		
Radiation, $\lambda/\text{\AA}$	Mo-K $\alpha$ , graphite monochromator, 0.71069		
Scanning range (deg)	$2.09 \leq \theta \leq 24.97$		
Scanning technique	$\omega$		
Scan step (deg)	$0.85 + 0.35\text{tg}\theta$		
Ranges of the indices reflections	$-5 \leq h \leq 10$ $-12 \leq k \leq 12$ $-6 \leq l \leq 12$		

added with intense stirring and cooling to  $-20^{\circ}\text{C}$  to an ethereal solution (50 mL) of ligand **1** (5.14 g, 16.45 mmol), which was prepared at the previous stage. The reaction mixture was allowed to warm to  $-20^{\circ}\text{C}$  and kept for 12 h. The white precipitate that formed was filtered off and washed three times on a filter with the same mixture of solvents. The resulting white powdered compound was dried *in vacuo* ( $10^{-3}$  Torr). Dilithium salt **3** was obtained in a yield of 4.91 g (12.32 mmol, 74.9%).

$^1\text{H}$  NMR (THF- $d_8$ ),  $\delta$ : 1.91 (s, 4 H,  $\text{CH}_2\text{Si}$ ); 6.01 (s, 2 H,  $=\text{CH}-\text{CH}_2\text{Si}$ ); 6.04 (d, 2 H, H-2,  $^3J_{\text{H}-\text{H}} = 3.2$  Hz); 6.47 (m, 4 H, H-5, H-6); 6.88 (d, 2 H, H-3,  $^3J_{\text{H}-\text{H}} = 3.2$  Hz); 7.32 (m, 2 H, H-7); 7.64 (m, 2 H, H-4).  $^{13}\text{C}$  NMR (THF- $d_8$ ),  $\delta$ : 20.50 ( $\text{CH}_2\text{Si}$ ); 95.14 (C-3); 98.26 (C-1); 114.33 (CH); 114.63 (CH); 119.40 (CH); 121.67 (CH); 125.99 (CH); 132.78 ( $=\text{CH}-\text{CH}_2\text{Si}$ ); 133.89 (C); 136.28 (C).

**Synthesis of *ansa*- $\{\eta^5, \eta^5-[1,1'-(1\text{-silacyclopent-3-en-1,1-diyl})\text{bis}(\text{indenyl})]\}$  dichlorozirconium (**1a,b**) (1,4- $\text{CH}_2\text{CH}=\text{CHCH}_2$ ) $\text{Si}(\text{C}_9\text{H}_6)_2\text{ZrCl}_2$ , *rac* : *meso* = 55 : 45) and crystallization of the pure *meso* form **1b**.** A suspension of dilithium salt **3** etherate (1.34 g, 3.36 mmol) and  $\text{ZrCl}_4$  (0.78 g, 3.36 mmol) in toluene (70 mL) was stirred for 1 day. The dry residue was repeatedly extracted with toluene. The toluene extract was concentrated. The crystalline yellow precipitate was filtered off from the mother liquor, washed with toluene and pentane, and dried *in vacuo* ( $10^{-3}$  Torr). The target complex **1a,b** was obtained as a mixture of the *rac* and *meso* forms in a ratio 55 : 45 in a yield of 1.02 g (2.17 mmol, 64.5%). Subsequent repeated fractional crystallization from dichloromethane gave the pure *meso* form **1b** in a yield of 0.26 g (0.53 mmol, 25.5%).

$^1\text{H}$  NMR of **1b** ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$ : 2.29 (br.s, 2 H,  $\text{CH}_2\text{Si}$ ); 2.64 (br.s, 2 H,  $\text{CH}_2\text{Si}$ ); 6.17 (d, 2 H, H-2,  $^3J_{\text{H}-\text{H}} = 3.5$  Hz); 6.30 (m, 2 H,  $=\text{CH}-\text{CH}_2\text{Si}$ ); 6.95 (d, 2 H, H-3,  $^3J_{\text{H}-\text{H}} = 3.5$  Hz); 6.93 (t, 2 H); 7.22 (t, 2 H); 7.51 (d, 2 H); 7.53 (d, 2 H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$ : 16.45 ( $\text{CH}_2\text{Si}$ ); 16.86 ( $\text{CH}_2\text{Si}$ ); 89.08 (C-1); 119.62 (CH); 119.85 (CH); 125.75 (CH); 126.06 (CH); 126.34 (CH); 127.54 (CH); 130.65 ( $=\text{CH}-\text{CH}_2\text{Si}$ ); 130.88 ( $=\text{CH}-\text{CH}_2\text{Si}$ ); 128.13 (C); 134.93 (C).

$^1\text{H}$  NMR of **1a** (as a 2 : 1 mixture with **1b**;  $\text{CD}_2\text{Cl}_2$ ),  $\delta$ : 2.37 (AB system, 2 H,  $\text{CH}_2\text{Si}$ ,  $^2J_{\text{H}-\text{H}} = 17.0$  Hz); 2.56 (AB system, 2 H,  $\text{CH}_2\text{Si}$ ,  $^2J_{\text{H}-\text{H}} = 17.0$  Hz); 6.11 (d, 2 H, H-2,  $^3J_{\text{H}-\text{H}} = 3.5$  Hz); 6.29 (s, 2 H,  $=\text{CH}-\text{CH}_2\text{Si}$ ); 6.90 (d, 2 H, H-3,  $^3J_{\text{H}-\text{H}} = 3.5$  Hz); 7.10 (t, 2 H); 7.39 (t, 2 H); 7.51 (d, 2 H); 7.60 (d, 2 H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$ : 16.99 ( $\text{CH}_2\text{Si}$ ); 87.94 (C-1); 117.95 (CH); 118.14 (CH); 124.38

(CH); 126.34 (CH); 127.18 (CH); 128.00 (CH); 130.70 ( $=\text{CH}-\text{CH}_2\text{Si}$ ); 125.89 (C); 133.79 (C).

**X-ray diffraction study of complex **1b**.** The crystallographic characteristics and the details of data collection and of the structure solution and refinement of complex **1b** are given in Table 5. The coordinates of nonhydrogen atoms and their equivalent isotropic thermal parameters are given in Table 1. The bond lengths and the selected bond angles are listed in Tables 2 and 3, respectively.

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