

## Synthesis and X-ray crystal structures of *rac*- and *meso*-2,2'-propylidene-bis(1-indenyl) zirconium dichlorides

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### Abstract

An improved synthesis of 2,2'-bis(1-indenyl)propane and the corresponding *ansa*-complexes of zirconium are reported. Synthesis of a mixture of *rac*- and *meso*-2,2'-propylidene-bis(1-indenyl)zirconium dichlorides involves a treatment of ZrCl<sub>4</sub> with bis[3-(trialkyltin)inden-1-yl]propane, where alkyl = ethyl, butyl, in toluene. This reaction gives the products in 92% yield and might be a convenient synthetic pathway to a number of straightforward *ansa*-metallocenes. Both *rac*- and *meso*-2,2'-propylidene-bis(1-indenyl)zirconium dichlorides were separated and isolated using simple work-up processes, and characterized by X-ray crystal structure analysis (*rac*-: *C*2/*c*; *a* = 15.903(3) Å, *b* = 11.105(2) Å and *c* = 11.520(2) Å; β = 121.61(3)°; *Z* = 4; *V* = 1732.6(5) Å<sup>3</sup>; *R* = 0.0350; *meso*-: *P*1̄; *a* = 9.739(2) Å, *b* = 12.798(4) Å and *c* = 15.322(4) Å; α = 101.18(2)°; β = 121.61(2)°; γ = 90.54(2)°, *Z* = 4; *V* = 1795.4(8) Å<sup>3</sup>; *R* = 0.0417).

**Keywords:** Metallocenes; Zirconium; Tin; Crystal structure

### 1. Introduction

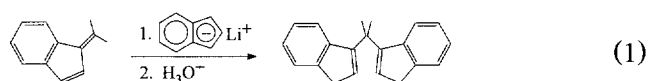
The design and synthesis of *ansa*-metallocenes of Group 4 elements are of considerable current interest for organometallic and polymer chemists in both academic and industrial laboratories [1,2]. This results from the particular catalytic properties of the compounds in stereospecific olefin polymerization and co-polymerization. A wide range of zirconium *ansa*-metallocenes traditionally have been prepared by the exchange reaction of ZrCl<sub>4</sub> with alkali-metal derivatives of the corresponding substituted cyclopentadienes [1]. This synthesis method is rather limited because of the low product yield, as well as being time-consuming because of the difficulties associated with the isolation and purification of the compounds. Here we describe a new straightforward selective route to the synthesis of *ansa*-metallocenes of zirconium. This reaction, involving the use of the corresponding organotin reagents, gives *rac*- and *meso*-2,2'-propylidene-bis(1-indenyl)zirconium dichlo-

rides in high yield (for a preliminary communication on this subject see Ref. [3]). This paper also includes descriptions of the improved synthesis of 2,2'-bis(1-indenyl)propane as well as the results of X-ray crystal structure analysis of the above-mentioned isomeric organozirconium compounds.

### 2. Results and discussion

#### 2.1. Synthesis of 2,2'-bis(1-indenyl)propane

2,2'-Bis(1-indenyl)propane was previously synthesized in moderate yield by the nucleophilic addition of indenyl lithium to the corresponding 2,2'-dimethylfulvene derivative of indene in THF (Eq. (1)) [4].



We found that the reaction of acetone with two equivalents of freshly distilled indene in the presence of

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#### 2.4. Molecular structures of *rac*- and *meso*-2,2'-propylidene-bis(1-indenyl)zirconium dichlorides

Fig. 1 shows two independent molecules **1**; Fig. 2 shows molecule **2**. It is seen that both independent molecules **1** represent a *meso* complex, whereas molecule **2** is a *racemate*. In both cases, the zirconium atom is coordinated by  $\eta^5$  cyclopentadienyl fragments of two indenyl groups of the ansa ligand and two chlorine atoms.

Molecules **1** and **2** have noticeable geometric distortions due to a short CMe<sub>2</sub> bridge between two indenyl fragments. The dihedral angle between the planes of the Cp rings is 108.3° and 108.5° in **1** and 109.1° in **2**, whereas, in the ordinary zirconocenes, it is commonly about 125°. The C(Cp)C(br)C(Cp) angle (100.1(3)° in **1** and 100.3(3)° in **2**) is significantly reduced in both compounds compared with the tetrahedral value (109.5°). The angles between the normals to each Cp plane and the line from the zirconium atom to the centroid of the corresponding Cp ring vary from 5.2 to

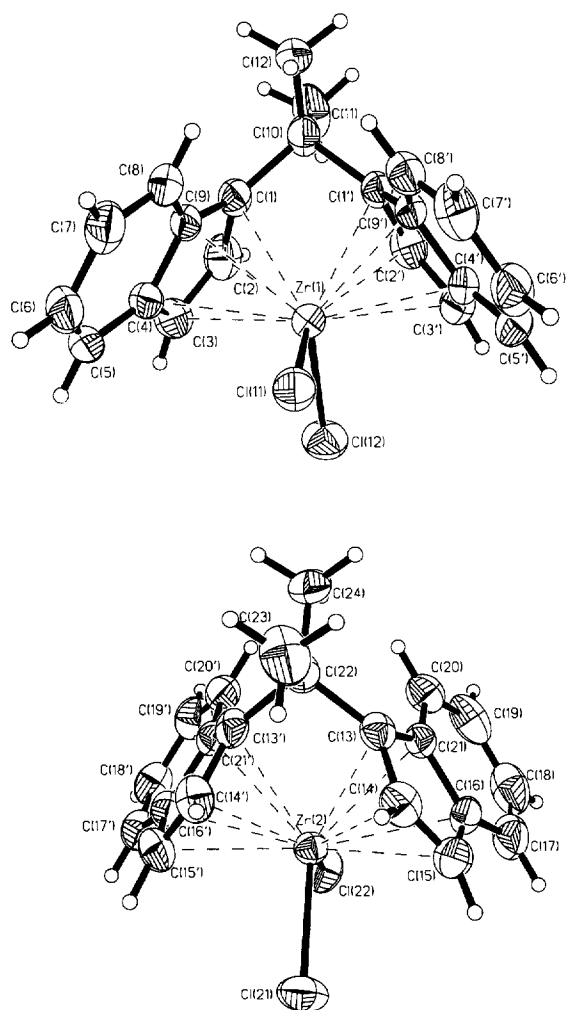


Fig. 1. ORTEP diagram of two independent molecules **1**.

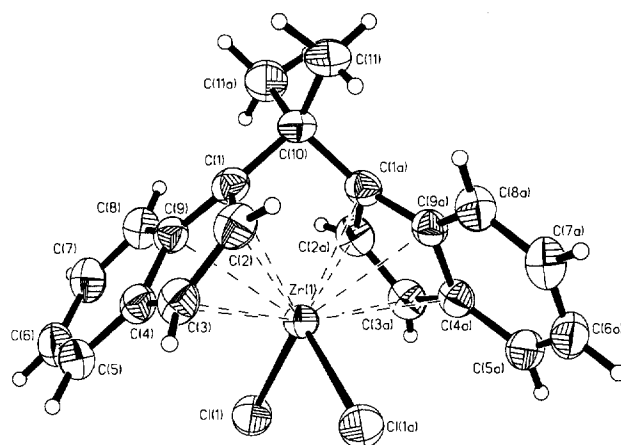


Fig. 2. ORTEP diagram of molecule **2**.

5.7° for **1** and are equal to 5.1° for **2**. In both structures, the bridging carbon atom between two indenyl radicals is displaced from the planes of two Cp fragments towards the zirconium atom. For **1** the displacements vary within 0.385–0.394 Å, and for **2** the displacement equals 0.396 Å; the angle between the corresponding Cp plane and the C(br)–C(Ph) bond equals 14.2–14.5° in **1** and 14.6° in **2**.

The Zr–C(Cp) distances are not equal for both Cp rings in **1** and **2**. In **1**, bond lengths Zr(1)–C(1) 2.428(4), Zr(1)–C(1') 2.427(4), Zr(2)–C(13) 2.433(4), and Zr(2)–C(13') 2.436(4) Å are the shortest, whereas, bond lengths Zr(1)–C(4) 2.627(4), Zr(1)–C(4') 2.620(4), Zr(2)–C(16) 2.614(4), and Zr(2)–C(16') 2.619(4) Å are the longest. A similar pattern of bond lengths is found in molecule **2**: the Zr(1)–C(1) bond (2.435(3) Å) is the shortest and Zr(1)–C(4) (2.615(3) Å) is the longest. The Zr–Cl bond lengths (2.397(1)–2.441(1) Å in **1** and 2.430(1) Å in **2**) have usual values. All of the above data show that the geometric distortions in the *rac*- and *meso*-complexes are almost identical.

### 3. Experimental details

All manipulations have been done either on the high vacuum line in all-glass apparatus equipped with polytetrafluoroethylene stopcocks or in an atmosphere of thoroughly purified argon using the standard Schlenk technique. THF was distilled over LiAlH<sub>4</sub>. Toluene was distilled over Na and kept over CaH<sub>2</sub>. Acetone (and acetone-*d*<sub>6</sub>) was dried with K<sub>2</sub>CO<sub>3</sub> and distilled. CH<sub>2</sub>Cl<sub>2</sub>, CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> were distilled over P<sub>4</sub>O<sub>10</sub> and kept over 3 Å molecular sieves. Et<sub>3</sub>SnNEt<sub>2</sub> and <sup>n</sup>Bu<sub>3</sub>SnNEt<sub>2</sub> were prepared according to the published procedures [15]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker AM 360 spectrometer.

### 3.1. 2,2'-bis(1-Indenyl)propane

A mixture of 11.6 g (0.10 mol) of freshly distilled indene, 2.9 g (0.05 mol) of acetone, 10.0 g (0.25 mol) of NaOH powder, and 0.44 g (0.002 mol) of 15-crown-5 in 50 ml of THF was stirred overnight. The brown suspension was mixed with ca. 100 cm<sup>3</sup> of ice. The mixture was neutralized with 50 ml of 10% HCl, and then ca. 50 ml of THF was added to dissolve the precipitate. The organic layer was separated, and the aqueous layer was washed with 3 × 30 ml of ether. The organic solvent was removed under reduced pressure. The brown viscous oil was treated with 70 ml of pentane. The resulting suspension was filtered, the product was washed with cold pentane, and dried in vacuum. This procedure yielded 6.2 g (46%) of pale yellow solid. Anal. Found: C, 92.67; H, 7.42. C<sub>21</sub>H<sub>20</sub>. Calc.: C, 92.60; H, 7.40%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 1.77 (s, 6H, Me), 3.41 (d,

*J* = 1.6 Hz, 4H, 3-H in C<sub>9</sub>H<sub>7</sub>), 6.63 (t, *J* = 2.2 Hz, 2H, 2-H in C<sub>9</sub>H<sub>7</sub>), 7.02 (m, 4H, 4,7-H<sub>2</sub> in C<sub>9</sub>H<sub>7</sub>), 7.38 (m, 4H, 5,6-H<sub>2</sub> in C<sub>9</sub>H<sub>7</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 28.43 (Me), 37.68 (CMe<sub>2</sub>), 38.54 (3-C in C<sub>9</sub>H<sub>6</sub>), 122.10, 124.41, 124.86, 126.23, 128.03 (2-C, 4-C, 5-C, 6-C, 7-C in C<sub>9</sub>H<sub>6</sub>), 144.89, 146.00, 151.31 (1-C, 3a-C, 7a-C in C<sub>9</sub>H<sub>6</sub>).

### 3.2. 2,2'-bis[3-(Triethyltin)inden-1-yl]propane

30.6 g (0.110 mol) of Et<sub>3</sub>SnNEt<sub>2</sub> was added dropwise for 0.5 h to a stirred solution of 15.0 g (0.055 mol) 2,2'-bis(1-indenyl)propane in 100 ml of THF at -35 °C. Then the mixture was warmed for 2 h to room temperature and stirred for 3 h. The solvent was concentrated under reduced pressure. The brown oil was continuously dried in vacuum to remove traces of THF. This procedure yielded analytically pure mixture of isomeric

Table 1  
Crystal data and structure refinement details for **1** and **2**

Compound	<b>1</b> ( <i>meso</i> -)	<b>2</b> ( <i>rac</i> -)
<b>Crystal parameters</b>		
Formula	C <sub>21</sub> H <sub>18</sub> Cl <sub>2</sub> Zr	C <sub>21</sub> H <sub>18</sub> Cl <sub>2</sub> Zr
Formula weight	432.47	432.47
Crystal system	Triclinic	Monoclinic
Crystal color; habit	orange-red; plate	orange; block
Crystal size (mm <sup>3</sup> )	0.26 × 0.12 × 0.54	0.22 × 0.28 × 0.33
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.739(2)	15.903(3)
<i>b</i> (Å)	12.798(4)	11.105(2)
<i>c</i> (Å)	15.322(4)	11.520(2)
$\alpha$ (deg)	101.18(2)	90
$\beta$ (deg)	106.16(2)	121.61(3)
$\gamma$ (deg)	90.55(2)	90
<i>V</i> (Å <sup>3</sup> )	1795.4(8)	1732.6(5)
<i>Z</i>	4	4
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.600	1.658
<i>F</i> (000)	872	872
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.909	0.942
<i>T</i> (K)	293	293
<b>Data collection and refinement (Mo K<math>\alpha</math>, <math>\lambda</math> = 0.71073 Å)</b>		
Scan mode	$\omega$	$\omega$
Max/min scan speed in $\omega$ (deg min <sup>-1</sup> )	8.2/1.2	8.2/1.2
Scan range $\omega$	1.0 ÷ 0.35 tan $\theta$	1.2 ÷ 0.35 tan $\theta$
$\theta$ range (deg)	2.18 to 26.97	2.37 to 29.96
Index ranges	-12 < <i>h</i> < 11 -16 < <i>k</i> < 16 0 < <i>l</i> < 19	-18 < <i>h</i> < 22 0 < <i>k</i> < 15 0 < <i>l</i> < 16
Reflections collected	7250	2447
Independent reflections	6999 ( <i>R</i> (int) = 0.0236)	2336 ( <i>R</i> (int) = 0.0492)
Refinement method (on <i>F</i> <sup>2</sup> )	full-matrix LS	full-matrix LS
Data/restraints/parameters	6999/0/434	2336/0/111
Goodness-of-fit	0.807	0.847
Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> 1 = 0.0417 <i>wR</i> 2 = 0.0967	<i>R</i> 1 = 0.0350 <i>wR</i> 2 = 0.0970
Extinction coefficient	0.0000(3)	0.0001(2)
Largest diff peak and hole (e Å <sup>-3</sup> )	0.464 and -0.734	0.983 and -0.924

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**

Atom	x	y	z	$U_{\text{eq}}^a$
Zr(1)	1547(1)	2622(1)	9693(1)	33(1)
Zr(2)	2581(1)	6871(1)	4725(1)	31(1)
Cl(11)	1619(1)	916(1)	8729(1)	44(1)
Cl(12)	-1018(1)	2864(1)	9214(1)	56(1)
Cl(21)	2107(1)	5225(1)	3559(1)	56(1)
Cl(22)	165(1)	7311(1)	4635(1)	47(1)
C(1)	3182(5)	3141(3)	11246(3)	39(1)
C(2)	1780(5)	3325(4)	11327(3)	49(1)
C(3)	986(5)	2349(4)	11155(3)	50(1)
C(4)	1884(5)	1524(4)	11010(3)	42(1)
C(5)	1654(5)	394(4)	10859(3)	52(1)
C(6)	2735(6)	-212(4)	10768(3)	57(1)
C(7)	4085(6)	239(4)	10809(3)	53(1)
C(8)	4359(5)	1301(3)	10937(3)	43(1)
C(9)	3263(4)	1994(3)	11051(3)	36(1)
C(10)	4156(5)	4005(3)	11113(3)	44(1)
C(11)	4027(7)	5091(4)	11719(3)	69(2)
C(12)	5736(5)	3799(4)	11358(3)	57(1)
C(1')	3480(4)	3993(3)	10074(3)	35(1)
C(2')	2193(5)	4490(3)	9749(3)	45(1)
C(3')	1589(5)	4096(4)	8801(3)	49(1)
C(4')	2516(4)	3377(3)	8489(3)	39(1)
C(5')	2456(6)	2803(4)	7592(3)	53(1)
C(6')	3542(6)	2189(4)	7487(3)	57(1)
C(7')	4692(6)	2100(4)	8246(3)	54(1)
C(8')	4788(5)	2615(3)	9117(3)	41(1)
C(9')	3699(4)	3296(3)	9278(3)	34(1)
C(13)	4567(4)	8187(3)	5034(3)	36(1)
C(14)	4582(5)	7449(3)	4228(3)	44(1)
C(15)	3412(5)	7529(4)	3486(3)	50(1)
C(16)	2636(5)	8373(4)	3794(3)	43(1)
C(17)	1389(5)	8819(4)	3321(4)	59(1)
C(18)	890(6)	9638(5)	3794(4)	68(2)
C(19)	1559(6)	10075(4)	4742(4)	62(1)
C(20)	2746(5)	9663(3)	5233(3)	45(1)
C(21)	3321(4)	8795(3)	4767(3)	35(1)
C(22)	5425(4)	8096(3)	6018(3)	41(1)
C(23)	6905(5)	7680(4)	6027(4)	66(2)
C(24)	5698(5)	9146(4)	6715(3)	58(1)
C(13')	4475(4)	7247(3)	6190(3)	37(1)
C(14')	4483(4)	6147(3)	5809(3)	43(1)
C(15')	3263(5)	5586(3)	5826(3)	43(1)
C(16')	2466(4)	6309(3)	6260(3)	36(1)
C(17')	1178(4)	6145(4)	6490(3)	44(1)
C(18')	654(5)	6986(4)	6942(3)	51(1)
C(19')	1362(5)	8007(4)	7174(3)	51(1)
C(20')	2575(5)	8207(3)	6956(3)	42(1)
C(21')	3190(4)	7350(3)	6483(3)	34(1)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

products in almost quantitative yield. Anal. Found: C, 58.43; H, 7.25.  $\text{C}_{33}\text{H}_{48}\text{Sn}_2$ . Calc.: C, 58.11; H, 7.09%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.94–1.14 (m, 12H,  $\text{CH}_2\text{Me}$ ), 1.32–1.44 (m, 18H,  $\text{CH}_2\text{Me}$ ), 2.04, 2.05, 2.06, and 2.10 (s, s, s, and s, 6H,  $\text{CMe}_2$ ), 4.33 and 4.36 (d,  $J = 2.0$  Hz,  $J(^1\text{H}-^{119}\text{Sn}) = 85.7$  Hz and d,  $J = 1.9$  Hz,  $J(^1\text{H}-^{119}\text{Sn}) = 85.1$  Hz, 2H, 3-H in  $\text{C}_9\text{H}_6$ ), 6.95 and 6.98 (d,  $J = 2.0$  Hz and d,  $J = 2.0$  Hz, 2H, 2-H in

$\text{C}_9\text{H}_6$ ), 7.16–7.31 (m, 4H, 4,7-H<sub>2</sub> in  $\text{C}_9\text{H}_6$ ), 7.59–7.71 (m, 4H, 5,6-H<sub>2</sub> in  $\text{C}_9\text{H}_6$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.71, 1.78, 1.84 ( $\text{CH}_2\text{CH}_3$ ), 10.89, 10.91 ( $\text{CH}_2\text{CH}_3$ ), 28.50, 28.60, 28.75, 29.03, 29.38 ( $\text{CMe}_2$ ), 38.01, 38.08, 38.12 ( $\text{CMe}_2$ ), 40.69, 40.73, 40.84 (3-C in  $\text{C}_9\text{H}_6$ ), 121.53, 121.62, 121.63, 121.84, 121.86, 121.88, 122.25, 122.29, 122.41, 122.59, 122.63, 122.80, 128.95, 129.23, 129.28 (2-C, 4-C, 5-C, 6-C, 7-C in  $\text{C}_9\text{H}_6$ ), 141.20, 141.31, 141.33, 143.66, 144.53, 144.70, 147.87, 148.00, 148.03 (1-C, 3a-C, 7a-C in  $\text{C}_9\text{H}_6$ ).

The synthesis of 2,2'-bis[3-(tributyltin)inden-1-yl]propane was performed in a similar manner.

### 3.3. The rac- and meso-2,2'-propylidene-bis(1-indenyl)zirconium dichlorides

A solution of 9.6 g (14 mmol) of 2,2'-bis[3-(triethyltin)inden-1-yl]propane in 20 ml of toluene was added dropwise for 1.5 h to a suspension of 3.2 g (14 mmol) of  $\text{ZrCl}_4$  in 30 ml of toluene. The mixture was stirred for 3 h at 90 °C and then cooled to 0 °C. The orange-red suspension was filtered. The orange-red crystalline solid was washed with  $4 \times 30$  ml of  $\text{CH}_2\text{Cl}_2$ , 70 ml of THF and dried. This procedure yields  $\text{CH}_2\text{Cl}_2$  solution of meso complex and 2.46 g (46%) of analytically pure **2**. Anal. Found: C, 58.24; H, 4.16.  $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{Zr}$ . Calc.: C, 58.32; H, 4.19%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.34 (s, 6H,  $\text{CMe}_2$ ), 6.16 (d,  $J = 3.5$  Hz, 2H, 2-H in  $\text{C}_9\text{H}_6$ ), 6.65 (dd,  $J = 3.5$  Hz, 2H, 3-H in  $\text{C}_9\text{H}_6$ ), 6.96–7.04 (m, 2H, 4-H in  $\text{C}_9\text{H}_6$ ), 7.23–7.31 (m, 2H, 7-H in  $\text{C}_9\text{H}_7$ ), 7.47 (dd,  $J = 8.8$  Hz, 2H, 5-H in  $\text{C}_9\text{H}_6$ ), 7.74 (dd,  $J = 9.1$  Hz, 2H, 6-H in  $\text{C}_9\text{H}_6$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  28.16 ( $\text{CMe}$ ), 37.58 ( $\text{CMe}_2$ ), 101.25 (1-C in  $\text{C}_9\text{H}_6$ ), 110.31 (2-C in  $\text{C}_9\text{H}_6$ ), 111.66 (3-C in  $\text{C}_9\text{H}_6$ ), 118.70 (7a-C in  $\text{C}_9\text{H}_6$ ), 123.85 (4-C in  $\text{C}_9\text{H}_6$ ), 124.50 (5-C in  $\text{C}_9\text{H}_6$ ), 124.67 (6-C in  $\text{C}_9\text{H}_6$ ), 124.71 (7-C in  $\text{C}_9\text{H}_6$ ), 130.63 (3a-C in  $\text{C}_9\text{H}_6$ ). The solvent from  $\text{CH}_2\text{Cl}_2$

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2**

Atom	x	y	z	$U_{\text{eq}}^a$
Zr(1)	0	2026(1)	2500	30(1)
Cl(1)	1323(1)	623(1)	3064(1)	47(1)
C(1)	-174(2)	3945(2)	1373(3)	36(1)
C(2)	-1074(2)	3317(3)	562(3)	42(1)
C(3)	-935(2)	2326(3)	-70(3)	43(1)
C(4)	60(2)	2318(3)	293(3)	38(1)
C(5)	582(3)	1552(3)	-99(3)	47(1)
C(6)	1555(3)	1755(3)	423(4)	53(1)
C(7)	2048(3)	2731(3)	1325(3)	49(1)
C(8)	1569(2)	3491(3)	1701(3)	42(1)
C(9)	549(2)	3315(3)	1204(3)	35(1)
C(10)	0	4829(4)	2500	41(1)
C(11)	-893(3)	5643(3)	2045(4)	63(1)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 4  
Bond lengths (Å) and angles (deg) for **1**

<b>Bond lengths</b>			
Zr(1)–Cl(11)	2.401(1)	Zr(1)–C(1)	2.428(4)
Zr(1)–C(1')	2.427(4)	Zr(1)–C(2)	2.436(4)
Zr(1)–Cl(12)	2.441(1)	Zr(1)–C(2')	2.445(4)
Zr(1)–C(9')	2.542(4)	Zr(1)–C(3)	2.535(4)
Zr(1)–C(3')	2.540(4)	Zr(1)–C(9)	2.551(4)
Zr(1)–C(4')	2.620(4)	Zr(1)–C(4)	2.627(4)
Zr(2)–Cl(22)	2.397(1)	Zr(2)–C(13)	2.433(4)
Zr(2)–Cl(21)	2.430(1)	Zr(2)–C(13')	2.436(4)
Zr(2)–C(14)	2.438(4)	Zr(2)–C(14')	2.443(4)
Zr(2)–C(15)	2.536(4)	Zr(2)–C(15')	2.542(4)
Zr(2)–C(21')	2.539(4)	Zr(2)–C(21)	2.542(4)
Zr(2)–C(16)	2.614(4)	Zr(2)–C(16')	2.619(4)
C(1)–C(2)	1.423(6)	C(1)–C(9)	1.447(6)
C(1)–C(10)	1.530(6)	C(2)–C(3)	1.402(6)
C(3)–C(4)	1.402(6)	C(4)–C(9)	1.446(6)
C(4)–C(5)	1.425(6)	C(5)–C(6)	1.337(7)
C(6)–C(7)	1.411(7)	C(7)–C(8)	1.348(6)
C(8)–C(9)	1.420(6)	C(10)–C(12)	1.517(7)
C(10)–C(1')	1.542(5)	C(10)–C(11)	1.541(6)
C(1')–C(2')	1.419(6)	C(1')–C(9')	1.434(5)
C(2')–C(3')	1.395(6)	C(3')–C(4')	1.406(6)
C(4')–C(9')	1.441(5)	C(4')–C(5')	1.412(6)
C(5')–C(6')	1.350(7)	C(6')–C(7')	1.397(7)
C(7')–C(8')	1.346(6)	C(8')–C(9')	1.423(6)
C(13)–C(14)	1.406(6)	C(13)–C(21)	1.452(5)
C(13)–C(22)	1.534(6)	C(14)–C(15)	1.388(7)
C(15)–C(16)	1.406(6)	C(16)–C(21)	1.445(6)
C(16)–C(17)	1.418(6)	C(17)–C(18)	1.331(8)
C(18)–C(19)	1.413(8)	C(19)–C(20)	1.364(7)
C(20)–C(21)	1.409(6)	C(22)–C(24)	1.515(6)
C(22)–C(13')	1.527(5)	C(22)–C(23)	1.538(6)
C(13')–C(14')	1.416(6)	C(13')–C(21')	1.442(5)
C(14')–C(15')	1.391(6)	C(15')–C(16')	1.401(6)
C(16')–C(21')	1.435(6)	C(16')–C(17')	11.418(6)
C(17')–C(18')	1.349(6)	C(18')–C(19')	1.405(7)
C(19')–C(20')	1.348(6)	C(20')–C(21')	1.425(6)
<b>Bond angles</b>			
Cl(11)–Zr(1)–Cl(12)	100.36(5)	Cl(22)–Zr(2)–Cl(21)	99.35(5)
C(2)–C(1)–C(9)	106.3(4)	C(2)–C(1)–C(10)	122.7(4)
C(9)–C(1)–C(10)	128.8(4)	C(1)–C(2)–C(3)	110.0(4)
C(4)–C(3)–C(2)	108.2(4)	C(3)–C(4)–C(9)	108.4(4)
C(3)–C(4)–C(5)	131.6(4)	C(9)–C(4)–C(5)	120.0(4)
C(6)–C(5)–C(4)	118.7(4)	C(5)–C(6)–C(7)	121.6(4)
C(8)–C(7)–C(6)	122.2(5)	C(7)–C(8)–C(9)	119.1(4)
C(8)–C(9)–C(4)	118.2(4)	C(8)–C(9)–C(1)	134.6(4)
C(4)–C(9)–C(1)	107.1(4)	C(1)–C(10)–C(12)	114.8(4)
C(1)–C(10)–C(1')	100.1(3)	C(12)–C(10)–C(1')	113.6(4)
C(1)–C(10)–C(11)	110.3(4)	C(12)–C(10)–C(11)	106.7(4)
C(1')–C(10)–C(11)	111.3(4)	C(2')–C(1')–C(9')	106.4(3)
C(2')–C(1')–C(10)	122.0(4)	C(9')–C(1')–C(10)	129.4(4)
C(3')–C(2')–C(1')	110.0(4)	C(2')–C(3')–C(4')	108.1(4)
C(3')–C(4')–C(9')	107.9(4)	C(3')–C(4')–C(5')	131.4(4)
C(9')–C(4')–C(5')	120.7(4)	C(6')–C(5')–C(4')	118.6(4)
C(5')–C(6')–C(7')	121.2(4)	C(8')–C(7')–C(6')	122.5(5)
C(7')–C(8')–C(9')	119.4(4)	C(1')–C(9')–C(4')	107.5(4)
C(1')–C(9')–C(8')	134.9(4)	C(4')–C(9')–C(8')	117.5(4)
C(14)–C(13)–C(21)	106.0(4)	C(14)–C(13)–C(22)	123.9(4)
C(21)–C(13)–C(22)	127.7(4)	C(15)–C(14)–C(13)	111.3(4)
C(16)–C(15)–C(14)	107.5(4)	C(15)–C(16)–C(21)	108.5(4)
C(15)–C(16)–C(17)	131.3(4)	C(21)–C(16)–C(17)	120.2(4)
C(18)–C(17)–C(16)	118.3(5)	C(17)–C(18)–C(19)	122.4(5)
C(20)–C(19)–C(18)	121.6(5)	C(19)–C(20)–C(21)	118.4(4)
C(20)–C(21)–C(16)	119.1(4)	C(20)–C(21)–C(13)	134.2(4)

Table 4 (continued)

C(16)–C(21)–C(13)	106.6(4)	C(24)–C(22)–C(13')	115.5(4)
C(24)–C(22)–C(13)	113.7(4)	C(13')–C(22)–C(13)	100.1(3)
C(24)–C(22)–C(23)	106.4(4)	C(13')–C(22)–C(23)	110.3(4)
C(13)–C(22)–C(23)	110.9(4)	C(14')–C(13')–C(21')	105.4(3)
C(14')–C(13')–C(22)	122.2(4)	C(21')–C(13')–C(22)	130.0(4)
C(15')–C(14')–C(13')	110.9(4)	C(16')–C(15')–C(14')	107.7(4)
C(15')–C(16')–C(21')	108.1(4)	C(15')–C(16')–C(17')	130.6(4)
C(21')–C(16')–C(17')	121.2(4)	C(18')–C(17')–C(16')	118.6(4)
C(17')–C(18')–C(19')	120.7(4)	C(20')–C(19')–C(18')	122.8(4)
C(19')–C(20')–C(21')	119.2(4)	C(16')–C(21')–C(20')	117.4(4)
C(16')–C(21')–C(13')	107.8(3)	C(20')–C(21')–C(13')	134.8(4)

solution was removed, red solid was washed with 2 × 10 ml pentane and dried. This procedure yielded 2.46 g (46%) of dark red crystalline **1**. Anal. Found: C, 58.47; H, 4.24. C<sub>21</sub>H<sub>18</sub>Cl<sub>2</sub>Zr. Calc.: C, 58.32; H, 4.19%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.18 (s, 3H, Me), 2.65 (s, 3H, Me), 6.08 (d, *J* = 3.4 Hz, 2H, 2-H in C<sub>9</sub>H<sub>6</sub>), 6.67 (dd, *J* = 3.5 Hz, 2H, 3-H in C<sub>9</sub>H<sub>6</sub>), 6.84–6.92 (m, 2H, 4-H in C<sub>9</sub>H<sub>6</sub>), 7.06–7.14 (m, 2H, 7-H in C<sub>9</sub>H<sub>7</sub>), 7.44 (dd, *J* = 8.7 Hz, 2H, 5-H in C<sub>9</sub>H<sub>6</sub>), 7.83 (dd, *J* = 9.0 Hz, *J* = 0.6 Hz, 2H, 6-H in C<sub>9</sub>H<sub>6</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 25.11 (CMe), 29.34 (CMe), 41.77 (CMe<sub>2</sub>), 103.76 (1-C in C<sub>9</sub>H<sub>6</sub>), 112.92 (2-C in C<sub>9</sub>H<sub>6</sub>), 113.61 (3-C in C<sub>9</sub>H<sub>6</sub>), 122.10 (7a-C in C<sub>9</sub>H<sub>6</sub>), 125.73 (4-C in C<sub>9</sub>H<sub>6</sub>), 125.98 (5-C in C<sub>9</sub>H<sub>6</sub>), 126.02 (6-C in C<sub>9</sub>H<sub>6</sub>), 126.41 (7-C in C<sub>9</sub>H<sub>6</sub>), 131.14 (3a-C in C<sub>9</sub>H<sub>6</sub>).

#### 3.4. X-ray diffraction study of rac- and meso-2,2'-propylidene-bis(1-indenyl)zirconium dichlorides

The details of the X-ray experiment and crystallographic parameters for **1** and **2** are given in Table 1.

Table 5  
Bond lengths (Å) and angles (deg) for **2**

Bond lengths			
Zr(1)–Cl(1)	2.4174(9)	Zr(1)–C(1)	2.435(3)
Zr(1)–C(2)	2.441(3)	Zr(1)–C(9)	2.531(3)
Zr(1)–C(3)	2.544(3)	Zr(1)–C(4)	2.615(3)
C(1)–C(2)	1.417(4)	C(1)–C(9)	1.443(4)
C(1)–C(10)	1.533(4)	C(2)–C(3)	1.399(5)
C(3)–C(4)	1.409(4)	C(4)–C(5)	1.416(5)
C(4)–C(9)	1.441(4)	C(5)–C(6)	1.353(5)
C(6)–C(7)	1.419(5)	C(7)–C(8)	1.351(5)
C(8)–C(9)	1.423(4)	C(10)–C(11)	1.526(4)
Bond angles			
Cl(1)–Zr(1)–Cl(1a)	99.76(5)	C(2)–C(1)–C(9)	105.9(3)
C(2)–C(1)–C(10)	123.1(2)	C(9)–C(1)–C(10)	128.4(2)
C(1)–C(2)–C(3)	110.4(3)	C(4)–C(3)–C(2)	108.1(3)
C(3)–C(4)–C(5)	131.6(3)	C(3)–C(4)–C(9)	107.6(3)
C(5)–C(4)–C(9)	120.8(3)	C(6)–C(5)–C(4)	118.8(3)
C(5)–C(6)–C(7)	121.1(3)	C(8)–C(7)–C(6)	121.6(3)
C(7)–C(8)–C(9)	120.1(3)	C(8)–C(9)–C(1)	134.4(3)
C(8)–C(9)–C(4)	117.6(3)	C(1)–C(9)–C(4)	107.9(3)
C(1)–C(10)–C(1a)	100.3(3)		

Symmetry transformations (a) used to generate equivalent atoms: –*x*, *y*, –*z* + 1/2.

The experimental reflections were collected at room temperature on an Enraf Nonius CAD4 diffractometer (Mo K $\alpha$  radiation, graphite monochromator). No absorption correction was applied for either structure.

The structures were solved by the direct method and refined by the full-matrix least squares on  $F^2$  in the anisotropic approximation. Crystals of **1** contain two independent molecules in the triclinic unit cell. The molecule in crystals of **2** occupies a special position at the two-fold axis in the monoclinic unit cell. In the difference Fourier syntheses, all of the hydrogen atoms were found in both structures. However, these atoms were calculated in the ideal positions and included in the further structure refinement as riding at the corresponding carbon atoms with isotropic thermal parameters  $U_{\text{iso}}$ , which is 1.5 times as much as the  $U_{\text{eq}}$  parameters of the corresponding carbon atom [16]. The final least squares on  $F^2$  were performed in the anisotropic approximation for the non-hydrogen atoms. All of the calculations were performed using SHELX76 [17] and SHELX93 [18] software.

Tables 2 and 3 give non-hydrogen atom coordinates and equivalent isotropic displacements for **1** and **2** respectively; Tables 4 and 5 give bond lengths and angles for **1** and **2** respectively.

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#### References

- [1] R.L. Halterman, *Chem. Rev.*, 92 (1992) 965 and references cited therein.
- [2] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 1143.
- [3] A.Z. Voskoboynikov, A. Yu. Agarkov, A.V. Churakov and L.G. Kuz'mina, *Izv. Rus. Akad. Nauk Ser. Khim.*, (1996) 765.
- [4] W. Spaleck, M. Antberg, V. Dolle, R. Klein, J. Rohmann and A. Winter, *New J. Chem.* 14 (1990) 499.

- [5] I.E. Nifant'ev, P.V. Ivchenko and M.V. Borzov, *Metalloorgan. Khim. (USSR)*, 5 (1992) 1371.
- [6] H.P. Fritz and C.G. Kreiter, *J. Organomet. Chem.*, 1 (1964) 323.
- [7] K. Jones and M.F. Lappert, *J. Organomet. Chem.*, 3 (1965) 295.
- [8] M.J. Bunker, A. DeCian and M.L.H. Green, *J. Chem. Soc. Chem. Commun.*, (1977) 59.
- [9] R.J. Burt, J. Chatt, G.J. Leigh, J.H. Teuben and A. Westerhaf, *J. Organomet. Chem.*, 129 (1977) C33.
- [10] P. Jutzi and M. Kuhn, *J. Organomet. Chem.*, 173 (1979) 221.
- [11] L.C. Hubert-Pfalzgraf and J.G. Riess, *Inorg. Chim. Acta*, 52 (1981) 231.
- [12] H. Wiesenfeldt, A. Reinmuth, E. Barsties, K. Evertz and H.-H. Brintzinger, *J. Organomet. Chem.*, 369 (1989) 359.
- [13] O.T. Beachley, J.F. Less, T.E. Glassman, M.R. Churchill and L.A. Buttvey, *Organometallics*, 9 (1990) 2488.
- [14] I.E. Nifant'ev, M.V. Borzov, A.V. Churakov, S.G. Mkoyan and L.O. Atovmyan, *Organometallics*, 11 (1992) 3942.
- [15] K. Jones and M.F. Lappert, *Organomet. Chem. Rev.*, 1 (1966) 67 and references cited therein.
- [16] N. Walker and D. Stuart, *Acta Crystallogr. Sect. A.*, 39 (1983) 158.
- [17] G.M. Sheldrick, *Acta Crystallogr. Sect. A.*, 46 (1990) 467.
- [18] G.M. Sheldrick, SHELX93, *Program for Refinement of Crystal Structure*, Universität Gottingen, 1993.