

## Notes

Molecular Structure of *rac-cis-1,4-2-Butenylenebis(1-indenyl)zirconium Dichloride*

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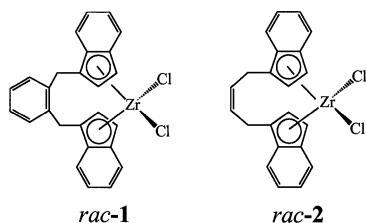
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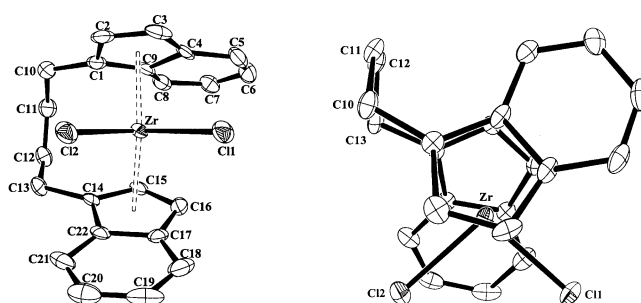
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*ansa*-Metallocene catalysts have been designed by variation of the transition metals, the bridging groups, and the  $\pi$ -ligands in order to improve the  $\alpha$ -olefin polymerization performance.<sup>1</sup> The presence of bridging groups restricts the mobility of the *ansa*-metallocene onto the growing polymer chain in an enantiomorphic site controlled process.<sup>2</sup> Slight structural variations of the bridging group are known to significantly affect the activity and the stereoregularity in  $\alpha$ -olefin polymerization reactions. In particular, the length of the bridging chain has an influence not only on the rigidity and the conformational geometry of  $\pi$ -ligands but also on the angle between the  $\pi$ -ligand centroids and the metal atom. Various bridging groups have been employed to investigate the influence of the corresponding *ansa*-metallocene catalysts on the polymerization behavior. The bridging unit is commonly oriented at the back side of the *ansa*-metallocene, *i.e.* disposed away from the  $\sigma$ -ligands at the pseudo-tetrahedrally coordinated group 4 metal center. The catalytically active site is known to be the open front side of the *ansa*-metallocene catalyst where the  $\sigma$ -ligands are located.

In previous work,<sup>3</sup> we reported the synthesis of a four-carbon bridged zirconocene, *rac-o*-phenylenedimethylenebis(indenyl)zirconium dichloride (*rac-1*), and its polymerization results. A single crystal of *rac-1* suitable for an X-ray diffraction study could not be obtained. We, therefore, prepared *rac-cis-1,4-2-butenylenebis(indenyl)zirconium dichloride* (*rac-2*), which has a similar bridging moiety to that of compound *rac-1*, in order to understand structural details of *rac-1*. Herein we report structural characterization of *rac-2*.



The overall molecular geometry and the atomic labeling scheme of *rac-2* are illustrated in Figure 1. Details of the crystallographic data and selected bond distances and angles are shown in Tables 1 and 2, respectively. The zirconium center of *rac-2* is coordinated to two substituted  $\eta^5$ -indenyl



**Figure 1.** Molecular structure of *rac-2* with atomic numbering scheme (left). Projection perpendicular to ZrCl(1)Cl(2) plane (right)

**Table 1.** Crystallographic data for complex *rac-2*

Formula	C <sub>22</sub> H <sub>18</sub> Cl <sub>2</sub> Zr
Fw	444.48
Crystal system	Triclinic
Space group	<i>P</i> 1
a, Å	9.748 (6)
b, Å	10.477 (2)
c, Å	9.084 (3)
$\alpha$ , deg	86.52 (2)
$\beta$ , deg	74.40 (4)
$\gamma$ , deg	91.48 (3)
V, Å <sup>3</sup>	891.1 (6)
Z	2
D <sub>calcd</sub> , g·m <sup>-3</sup>	1.657
temp, K	293
crystal size, mm	0.66×0.36×0.12
Radiation	Graphite-monochromated MoK $\alpha$
$\mu$ , mm <sup>-1</sup>	0.918
scan mode	$\omega/2\theta$
2 $\theta$ <sub>max</sub> , deg	50
no. of unique reflns	2478
no. of reflns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	2636
no. of params	226
<i>R</i> <sup>a</sup>	0.058
<i>R</i> <sub>w</sub> <sup>b</sup>	0.132
GOF <sup>c</sup>	1.05

<sup>a</sup>*R* =  $\sum(|F_o| - |F_c|) / \sum|F_o|$ . <sup>b</sup>*R*<sub>w</sub> =  $[\sum(|F_o| - |F_c|)^2 / \sum|F_o|^2]^{1/2}$ . <sup>c</sup>GOF =  $[\sum(|F_o| - |F_c|)^2 / (\text{No. of reflns} - \text{No. of params})]^{1/2}$

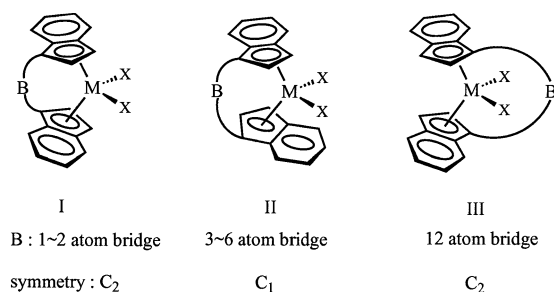
**Table 2.** Selected bond distances (Å) and bond angles (deg) for *rac-2* with estimated standard deviations

Bond distances			
Zr-Cl(1)	2.437(2)	Zr-C(16)	2.461(7)
Zr-Cl(2)	2.417(2)	Zr-C(17)	2.604(7)
Zr-C(1)	2.549(7)	Zr-C(22)	2.676(7)
Zr-C(2)	2.494(7)	C(10)-C(11)	1.505(1)
Zr-C(3)	2.450(7)	C(11)-C(12)	1.324(1)
Zr-C(4)	2.554(7)	C(12)-C(13)	1.480(1)
Zr-C(9)	2.637(8)	Zr-Ind(Cen) <sup>a</sup>	2.23(2)
Zr-C(14)	2.538(7)	Zr-Ind(Cen)	2.25(2)
Zr-C(15)	2.481(7)		
Bond angles			
Cl(1)-Zr-Cl(2)	97.1(3)	Ind(Cen)-Zr-Ind(Cen)	129.8(2)
C(10)-C(11)-C(12)	124.8(8)	Ind-Ind <sup>b</sup>	47.3(2)
C(11)-C(12)-C(13)	125.8(8)		

<sup>a</sup>Cen = ring centroid. <sup>b</sup>Interplanar angle between the two indenyl ligands.

(Ind) ligands and two chlorides in a pseudotetrahedral environment, in which Ind(Cen)-Zr-Ind(Cen) angle is 129.8(2)<sup>o</sup> and Cl-Zr-Cl bond angle is 97.1(3)<sup>o</sup> (Cen=ring centroid). The Zr-Cl bond lengths are 2.437(2) and 2.417(2) Å, and the Zr-Ind(Cen) lengths are 2.23(2) Å and 2.25(2) Å. The dihedral angle between two indenyl rings is 47.3(2)<sup>o</sup>. These values are in the typical range observed for many zirconium dichloride complexes. The two indenyl moieties are twisted with respect to each other, presumably, due to the significant strain by the 2-butenyl bridging group. One indenyl six-membered ring is oriented forward the open front side of the ZrCl<sub>2</sub> group, the other six-membered ring backward, and the 2-butenyl bridging group is placed in a side position (see the right view of Figure 1). Consequently, *rac-2* possesses a crystallographically imposed C<sub>1</sub> symmetry with two inequivalent indenyl ligands. The <sup>1</sup>H NMR spectrum of *rac-2*, however, has previously shown that the two indenyl ligands are equivalent in solution on the NMR time scale.<sup>3</sup> This observation admits two possible explanations that either *rac-2* exists as a C<sub>2</sub>-symmetric structure in solution or it undergoes rapid conformational interchange between two equivalent C<sub>1</sub> structures. This phenomenon has also been previously observed with *rac*-<sup>n</sup>Pr(IndH<sub>4</sub>)TiCl<sub>2</sub> (IndH<sub>4</sub>=tetrahydroindenyl)<sup>4</sup> and *rac*-(Me<sub>2</sub>SiOSiMe<sub>2</sub>)(Ind)<sub>2</sub>ZrCl<sub>2</sub><sup>5</sup> complexes.

Structural features of known racemic *ansa*-metallocenes with various bridging groups can be classified as shown in Scheme 1. Racemic *ansa*-metallocenes with one- (CH<sub>2</sub>=, Me<sub>2</sub>C= or Me<sub>2</sub>Si=) or two-atom bridge possess a C<sub>2</sub>-sym-

**Scheme 1**

metric ligand system (see I in Scheme 1), in which the bridging unit is oriented at the back of the bent-metallocene wedge and thus the active site ( $\sigma$ -ligand sites) is widely open resulting in high activity for isospecific propylene polymerization. Structurally characterized examples include *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>,<sup>6</sup> *rac*-CH<sub>2</sub>(IndH<sub>4</sub>)<sub>2</sub>TiCl<sub>2</sub>,<sup>7</sup> *rac*-<sup>n</sup>Pr(Ind)<sub>2</sub>ZrCl<sub>2</sub>,<sup>8</sup> *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>,<sup>9</sup> *rac*-(HC(CH<sub>3</sub>)(CH<sub>3</sub>)CH)(Ind)<sub>2</sub>ZrCl<sub>2</sub>,<sup>10</sup> and *rac*-( $\overline{\text{CH}}(\text{CH}_2)_4\overline{\text{CH}}$ )(IndH<sub>4</sub>)<sub>2</sub>TiCl<sub>2</sub>.<sup>11</sup> Those with three- to six-atom bridge, however, display an unsymmetrical (C<sub>1</sub>) arrangement of the ligand system due to the significant strain imposed by the bridging moiety (see II). The bridge is no longer found in the back of the molecule, but rather bulges to one side. As a result, the indenyl rings are twisted with respect to each other and one of the rings is directed toward the  $\sigma$ -ligand side, which results in reduced catalytic activities due to shielding of the catalytically active site. Previously reported complexes with three- to six-atom bridge are *rac*-<sup>n</sup>Pr(IndH<sub>4</sub>)<sub>2</sub>TiCl<sub>2</sub><sup>4</sup> and *rac*-(Me<sub>2</sub>SiOSiMe<sub>2</sub>)(Ind)<sub>2</sub>ZrCl<sub>2</sub><sup>5</sup> (three-atom bridge), *rac*-(Me<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>)(Ind)<sub>2</sub>ZrCl<sub>2</sub><sup>6</sup>, *rac*-( $\overline{\text{CH}_2\text{HC}}(\overline{\text{CH}_2})_3\overline{\text{CHCH}_2}$ )(Ind)<sub>2</sub>TiCl<sub>2</sub>,<sup>12</sup> and *rac*-( $\overline{\text{CH}_2\text{HC}}(\overline{\text{OCMe}_2\text{OCHCH}_2})$ )(IndH<sub>4</sub>)<sub>2</sub>ZrCl<sub>2</sub><sup>13</sup> (four-atom bridge), and [(R)-(-)-2,2'-bis(1-indenylmethyl)-1,1'-binaphthyl]TiCl<sub>2</sub><sup>14</sup> (six-atom bridge). Erker and coworkers have recently reported a twelve-carbon bridged *ansa*-zirconocene, *rac*-1,12-dodecanediylbis(3-indenyl)zirconium dichloride,<sup>15</sup> in which the long bridging dodecamethylene chain is unusually oriented in the front side of the *ansa*-metallocene (see III). This molecule has approximate C<sub>2</sub> symmetry. The (-CH<sub>2</sub>)<sub>12</sub> unit occupies a narrow band in the center of the open front side, which is also arranged in a C<sub>2</sub> symmetric conformation.

In conclusion, the molecular structure of complex *rac-2* shows an unsymmetrical C<sub>1</sub> geometry in which the two indenyl rings are twisted with respect to each other and active site is shielded by one of the six-membered ring of the indenyl moiety owing to the strain of the long *cis*-2-butenyl bridge. These structural features may explain that the previously reported *rac-1*/MAO (methylaluminoxane) catalytic system<sup>3</sup> has revealed a low activity and stereoregularity in propylene polymerization due to the unsymmetric nature and the rapid conformational change of *rac-1*, which are caused by the four-carbon *o*-phenylenedimethylene bridge.

## Experimental Section

**Data collection and structure solution of *rac-2*.** Compound *rac-2* was prepared by the procedures reported previously.<sup>3</sup> Single crystals of *rac-2* were obtained by slow recrystallization from chloroform at -20 °C. A yellow crystal with approximate dimensions 0.66×0.36×0.12 mm was sealed under argon in a thin walled glass capillary. Preliminary examination and data collection were performed using an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromated MoK $\alpha$  radiation ( $\lambda=0.71069$  Å) at 293 K. Unit cell parameters and orientation matrices were determined by least-square method of 9 reflections with 11.48<sup>o</sup> <  $\theta$  < 14.09<sup>o</sup>. Intensity data for 2636 independent reflections in the range -10 ≤ h ≤ 10, 0 ≤ k ≤ 11, -9 ≤ l ≤ 9 were col-

**Table 3.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^2$ ) for *rac-2*

atom	x	y	z	$U_{eq}^a$
Zr	3177(1)	2902(1)	3978(1)	3.1(1)
Cl(1)	5141(2)	2277(2)	5015(3)	5.1(1)
Cl(2)	2042(2)	4240(2)	5993(3)	5.1(1)
C(1)	2943(8)	4294(7)	1744(9)	3.8(2)
C(2)	3697(9)	5060(8)	2586(9)	4.9(2)
C(3)	5003(9)	4489(8)	2517(1)	5.0(2)
C(4)	5130(7)	3490(8)	1505(9)	4.2(2)
C(5)	6185(9)	2595(1)	998(1)	5.8(3)
C(6)	6057(1)	1807(1)	-96(12)	6.4(3)
C(7)	4873(9)	1826(9)	-715(10)	5.5(2)
C(8)	3805(8)	2631(8)	-181(9)	4.5(2)
C(9)	3860(7)	3447(7)	991(9)	3.8(2)
C(10)	1555(8)	4796(8)	1484(1)	5.0(2)
C(11)	691(8)	3785(8)	978(1)	5.0(2)
C(12)	-130(8)	2875(8)	1901(1)	4.9(2)
C(13)	-327(8)	2678(8)	3573(1)	4.6(2)
C(14)	799(7)	1856(7)	3978(9)	3.4(2)
C(15)	1891(7)	1230(7)	2979(9)	3.4(2)
C(16)	2712(8)	602(7)	3815(9)	3.9(2)
C(17)	2074(8)	724(7)	5389(9)	3.8(2)
C(18)	2393(1)	287(8)	6756(1)	5.9(3)
C(19)	1512(1)	569(1)	8140(1)	6.8(3)
C(20)	287(1)	1288(9)	8208(1)	6.3(3)
C(21)	-57(9)	1767(8)	6945(1)	5.3(2)
C(22)	847(7)	1482(7)	5495(9)	3.6(2)

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

**Table 4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^2$ ) for *rac-2*

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Zr	2.1(1)	3.2(1)	4.9(1)	0.3(1)	-0.5(1)	-0.6(1)
Cl(1)	3.4(1)	6.4(1)	5.7(1)	1.2(1)	-1.8(1)	-0.2(1)
Cl(1)	3.8(1)	4.4(1)	6.6(2)	-1.6(1)	-0.2(1)	-0.7(1)
C(1)	3.5(4)	3.3(4)	4.1(5)	0.9(4)	-0.7(1)	-1.0(4)
C(2)	5.4(6)	3.0(4)	5.2(5)	1.1(4)	0.2(4)	-1.4(4)
C(3)	4.1(5)	6.0(6)	5.0(5)	1.7(5)	-1.8(4)	-3.2(4)
C(4)	1.7(4)	5.7(6)	4.2(5)	1.9(4)	0.3(3)	-1.0(4)
C(5)	2.3(4)	7.2(7)	6.0(6)	2.7(5)	-0.5(4)	-0.1(5)
C(6)	4.1(5)	6.8(7)	6.7(7)	1.3(5)	0.9(5)	1.4(5)
C(7)	4.3(5)	6.2(6)	4.6(5)	0.6(4)	1.0(4)	0.0(4)
C(8)	3.0(4)	5.5(5)	4.5(5)	1.2(4)	-0.9(4)	0.1(3)
C(9)	1.8(4)	4.4(5)	4.7(5)	1.7(4)	-0.7(3)	-1.2(3)
C(10)	3.6(5)	4.3(5)	6.7(6)	1.2(4)	-0.8(4)	-0.8(4)
C(11)	3.6(5)	5.4(5)	6.2(6)	1.1(5)	-2.1(4)	0.5(4)
C(12)	2.3(4)	5.7(5)	6.7(6)	-0.1(5)	-1.6(4)	0.4(4)
C(13)	1.8(4)	4.8(5)	7.1(6)	-0.1(4)	-1.0(4)	-0.1(3)
C(14)	1.9(4)	2.9(4)	4.8(5)	0.2(3)	0.0(3)	-1.0(3)
C(15)	2.7(4)	3.0(4)	3.9(4)	-0.3(3)	-0.1(3)	-1.1(3)
C(16)	3.4(4)	2.8(4)	5.3(5)	-0.4(4)	-0.9(4)	0.1(3)
C(17)	3.8(4)	2.5(4)	4.9(5)	1.0(4)	-1.3(4)	-1.2(3)
C(18)	6.0(6)	3.9(5)	7.9(7)	2.4(5)	-3.1(6)	-1.5(4)
C(19)	9.6(8)	6.4(7)	4.1(6)	1.4(5)	-2.0(6)	-4.7(6)
C(20)	8.2(8)	6.1(6)	4.1(6)	-0.7(5)	-0.4(5)	-3.0(6)
C(21)	4.4(5)	5.0(5)	5.0(6)	-0.9(4)	1.0(4)	-2.1(4)
C(22)	2.7(4)	3.0(4)	4.5(5)	0.1(3)	-0.3(3)	-1.6(3)

$U_{ij}$  = The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [U_{11}h^2a^*2 + U_{22}k^2b^*2 + U_{33}l^2c^*2 + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*]$

lected using  $\omega/2\theta$  scan mode,  $\omega$ -scan angle =  $(0.8 + 0.35 \tan\theta)^\circ$ ,  $2\theta_{max} = 50^\circ$ . Two standard reflections showed less than

3.0% variation in intensity over the course of data collection. Lorentz and polarization corrections were applied to the intensity data. An empirical absorption correction was also applied to the data on the basis of  $\phi$  scans. All the calculations were carried out using the SHELXTL system of computer program.<sup>16</sup> The structure was solved by direct methods<sup>16a</sup> and refined by the full matrix least-square methods employing unit weights.<sup>16b</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were generated at calculated positions. Final reliability factors for 2478 unique observed reflections [ $I > 2\sigma(I)$ ] were  $R = 0.058$  and  $R_w = 0.132$ . The final residual values and structure refinement parameters are listed in Table 1. The atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms are listed in Tables 3 and 4, respectively.

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