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Acta Cryst. (1995). C**51**, 1488–1490

Racemic Dichloro{(*R*,*R*)-3,3′-(dimethylsilanediyl)bis[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-1-indenyl]}zirconium

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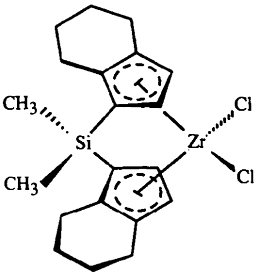
(*Received* 14 *November* 1994; *accepted* 3 *January* 1995)

Abstract

The structure of the title compound, $[(CH_3)_2Si(C_9H_{10})_2ZrCl_2]$ has been determined. The coordination geometry about the Zr atom is that of a distorted tetrahedron formed by the two Cl atoms and the centroids of the two silicon-bridged tetrahydroindenyl ligands. The Zr—Cl distances are 2.446 (2) and 2.437 (2) Å, and the Zr—C distances vary from 2.444 (4) to 2.639 (4) Å.

Comment

Chiral complexes of titanium, zirconium and hafnium incorporating two appropriately substituted cyclopentadienyl ligands are finding increasing application in enantioselective synthesis and stereoselective polymerization (Ellis *et al.*, 1993). For practical applications of metallocene-based olefin polymerization catalysts, further improvements in their catalytic activities and in the molar masses of their polyolefin products would be desirable. Previous studies on the activation of complexes of this type by methylaluminoxane (MAO) have shown that increased catalytic activities are associated with the presence of the aromatic six-membered rings in ethylenebis(1-indenyl)zirconium dichloride, as compared with its hydrogenated congener (Stehling *et al.*, 1994). In general, variations in the structures of bridged metallocenes give information on the correlation between metallocene structure and polymerization result, *e.g.* activity of the catalyst, average molar mass and chain microstructure of the polymer (Spaleck *et al.*, 1990; Kaminsky, 1994). We are systematically studying silicon-bridged bis(indenyl) metallocene complexes.



The catalytic properties of both the title complex (Fig. 1) and the non-hydrogenated congener have been discussed (Spaleck *et al.*, 1992). The polar activation in copolymerization of propylene and a phenolic polymer stabilizer when using the hydrogenated congener and MAO was recently reported (Wilén & Näsman, 1994). The crystallographic structure of racemic dichloro{(*R*,*R*)-3,3′-(dimethylsilanediyl)bis[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-1-indenyl]}zirconium, (I), has not been reported. In order to compare its structure with other new silane-bridged met-

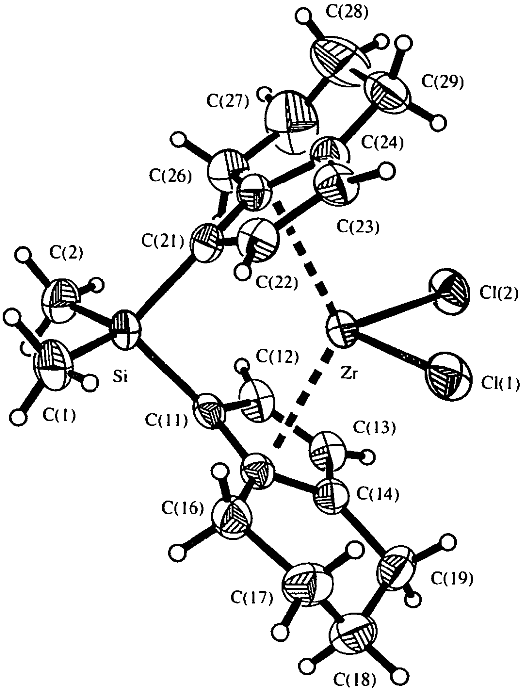


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

allocenes prepared in this and other laboratories, and to correlate the structural information with polymerization results, we report the structure of the title compound, (I).

The Zr^{IV} ion is η^5-bonded to the two silicon-bridged tetrahydroindenyl ligands and σ-bonded to two Cl ligands, adopting the familiar pseudotetrahedral '*ansa*-metallocene' configuration (Smith, Von Seyerl, Huttner & Brintzinger, 1979). The title compound is, in all essential features, isostructural with its non-hydrogenated (Spaleck *et al.*, 1992) congener (Table 3). The geometry around the Zr atom is comparable to that of similar silicon-bridged metallocenes (Burger, Hortmann, Diebold & Brintzinger, 1991; Stehling *et al.*, 1994; Luttikhedde, Leino, Näsman, Ahlgrén & Pakkanen, 1995). The Cp(1)—Zr—Cp(2) angle of 126.4 (2)° is comparable with 127.8° found in the corresponding non-hydrogenated congener (Spaleck *et al.*, 1992).

Experimental

The title compound, *rac*-$[(CH_3)_2Si(C_9H_{10})_2ZrCl_2]$, was obtained by hydrogenation of *rac*-$[(CH_3)_2Si(C_9H_6)_2ZrCl_2]$ (Herrmann, Rohrmann, Herdtweck, Spaleck & Winter, 1989) as described previously (Luttikhedde *et al.*, 1995) and identified by its ^1H and ^{13}C NMR spectra. ^1H NMR ($CDCl_3$): δ 6.65 (*d*, ^3J = 3.0 Hz, 2H), 5.49 (*d*, ^3J = 3.0 Hz, 2H), 2.96 (*ddd*, ^3J = 16.5, 7.9, 6.1 Hz, 2H), 2.70 (*dt*, ^3J = 16.5, 5.8 Hz, 2H), 2.58 (*ddd*, ^3J = 16.5, 7.9, 6.1 Hz, 2H), 2.33 (*dt*, ^3J = 16.5, 5.8 Hz, 2H) 2.00–1.91 (*m*, 2H), 1.84–1.74 (*m*, 2H), 1.62–1.46 (*m*, 4H), 0.76 p.p.m. (*s*, 6H). ^{13}C NMR ($CDCl_3$): δ 138.5, 128.8, 125.3, 112.7, 102.8, 26.2, 24.4, 22.4, 22.0, −2.1 p.p.m. Single crystals were obtained by slowly cooling a concentrated toluene solution to 258 K.

Crystal data

$[ZrCl_2(C_{20}H_{26}Si)]$
$M_r = 456.64$
Monoclinic
$P2_1/c$
$a = 10.471\ (5)$ Å
$b = 16.433\ (5)$ Å
$c = 11.426\ (4)$ Å
$\beta = 92.67\ (3)°$
$V = 1965\ (1)$ Å^3
$Z = 4$
$D_x = 1.543$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.7–15.7°$
$\mu = 0.88$ mm^{-1}
$T = 293$ K
Plate
0.40 × 0.40 × 0.15 mm
Green

Data collection

Nicolet *R*3*m* diffractometer
ω scans
Absorption correction: none
6235 measured reflections
5765 independent reflections
3695 observed reflections $[F > 4\sigma(F)]$
$R_{int} = 0.038$

$\theta_{max} = 30°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 23$
$l = -16 \rightarrow 16$
2 standard reflections monitored every 98 reflections
intensity decay: 3%

Refinement

Refinement on *F*
$R = 0.047$
$wR = 0.050$
$S = 1.25$
3695 reflections
217 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Zr	0.1779 (1)	0.3673 (1)	0.3188 (1)	0.028 (1)
Cl(1)	−0.0209 (1)	0.3460 (1)	0.4188 (1)	0.049 (1)
Cl(2)	0.2438 (1)	0.2253 (1)	0.3114 (1)	0.048 (1)
Si	0.2912 (1)	0.5467 (1)	0.2348 (1)	0.035 (1)
C(1)	0.2083 (5)	0.6441 (3)	0.2626 (5)	0.054 (2)
C(2)	0.4387 (5)	0.5645 (3)	0.1547 (4)	0.053 (2)
C(11)	0.1852 (4)	0.4691 (2)	0.1595 (3)	0.030 (1)
C(12)	0.2334 (4)	0.3940 (2)	0.1170 (3)	0.035 (1)
C(13)	0.1315 (4)	0.3384 (2)	0.0997 (3)	0.037 (1)
C(14)	0.0201 (4)	0.3765 (3)	0.1333 (3)	0.033 (1)
C(15)	0.0518 (4)	0.4565 (2)	0.1718 (3)	0.031 (1)
C(16)	−0.0488 (4)	0.5180 (3)	0.2025 (4)	0.041 (1)
C(17)	−0.1819 (4)	0.4799 (3)	0.2076 (4)	0.049 (2)
C(18)	−0.2080 (5)	0.4166 (3)	0.1129 (4)	0.051 (2)
C(19)	−0.1158 (4)	0.3455 (3)	0.1236 (4)	0.045 (1)
C(21)	0.3181 (4)	0.4848 (2)	0.3712 (3)	0.032 (1)
C(22)	0.2265 (4)	0.4774 (3)	0.4588 (4)	0.038 (1)
C(23)	0.2540 (5)	0.4068 (3)	0.5272 (3)	0.040 (1)
C(24)	0.3632 (4)	0.3694 (3)	0.4834 (3)	0.038 (1)
C(25)	0.4010 (4)	0.4155 (2)	0.3863 (4)	0.034 (1)
C(26)	0.5208 (4)	0.3964 (3)	0.3227 (4)	0.045 (1)
C(27)	0.5794 (6)	0.3178 (4)	0.3622 (7)	0.085 (3)
C(28)	0.5697 (6)	0.2971 (4)	0.4848 (6)	0.081 (3)
C(29)	0.4377 (5)	0.2987 (3)	0.5324 (4)	0.053 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cp(1) and Cp(2) refer to the centroids of the C(11)—C(12)—C(13)—C(14)—C(15) and C(21)—C(22)—C(23)—C(24)—C(25) rings, respectively.

Zr—Cl(1)	2.446 (2)	Zr—Cl(2)	2.437 (2)
Zr—C(11)	2.477 (4)	Zr—C(21)	2.483 (4)
Zr—C(12)	2.444 (4)	Zr—C(22)	2.453 (4)
Zr—C(13)	2.571 (4)	Zr—C(23)	2.559 (4)
Zr—C(14)	2.631 (4)	Zr—C(24)	2.639 (4)
Zr—C(15)	2.551 (4)	Zr—C(25)	2.552 (4)
Si—C(1)	1.856 (5)	Si—C(2)	1.855 (5)
Si—C(11)	1.874 (4)	Si—C(21)	1.871 (4)
Zr—Cp(1)	2.231 (4)	Zr—Cp(2)	2.232 (4)
Cl(1)—Zr—Cl(2)	97.3 (1)	Cp(1)—Zr—Cp(2)	126.4 (2)
C(1)—Si—C(2)	110.8 (2)	C(11)—Si—C(21)	94.3 (2)
C(1)—Si—C(11)	113.2 (2)	C(2)—Si—C(21)	113.6 (2)
C(1)—Si—C(21)	112.3 (2)	C(2)—Si—C(11)	111.7 (2)

Table 3. *Selected bond distances* (Å) *and angles* (°) *for* $[(CH_3)_2Si(C_9H_6)_2ZrCl_2]$ *and* $[(CH_3)_2Si(C_9H_{10})_2ZrCl_2]$

	$(CH_3)_2Si(C_9H_6)_2ZrCl_2$*	$(CH_3)_2Si(C_9H_{10})_2ZrCl_2$
Zr—Cl†	2.4314 (2)	2.441 (2)
Zr—C‡	2.470 (1)–2.659 (1)	2.444 (4)–2.639 (4)
Zr—Cp†	2.241	2.231 (4)
Si—C(11); Si—C(21)†	1.871 (1)	1.872 (4)
C—C§	1.396 (1)–1.446 (1)	1.394 (6)–1.438 (6)

Cl(1)—Zr—Cl(2)	98.76 (1)	97.3 (1)
Cp(1)—Zr—Cp(2)	127.8	126.4 (2)
C(1)—Si—C(2)	111.2 (1)	110.8 (2)
C(11)—Si—C(21)	94.57 (6)	94.3 (2)

* Herrmann *et al.* (1989).
† Average.
‡ Zr η^5-bonded C distances, minimum–maximum.
§ Cp C—C bond distance, minimum–maximum.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. C(27) and C(28) in Cp(2) show large displacement parameters indicating a slight disorder in the structure. H atoms were placed with idealized geometries (C—H = 0.96 Å) riding on their respective C atoms with fixed $U = 0.08$ Å^2.

Data collection: *P*3 *Data Collection Software* (Siemens, 1990). Cell refinement: *P*3 *Data Collection Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Structure solution: *SHELXTL-Plus*. Structure refinement: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Preparation of material for publication: *SHELXTL-Plus*.

HJGL, RPL and JHN wish to thank the Finnish Technology Development Centre (TEKES) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1236). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1490–1494

Molecular Stereochemistry of [$Fe^{III}(TPP)(OCOCF_3)$]

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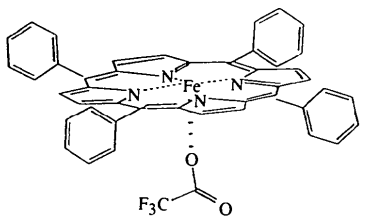
(*Received* 7 *October* 1993; *accepted* 1 *March* 1995)

Abstract

(*meso*-Tetraphenylporphinato)(trifluoroacetato)iron(III), [$Fe(C_2F_3O_2)(C_{44}H_{28}N_4)$], consists of a central Fe atom equatorially coordinated to four pyrrole N atoms and axially coordinated to an O atom of the trifluoroacetate group. The average Fe—N bond distance is 2.054 (5) Å and the Fe atom is displaced 0.483 (1) Å from the porphinato plane. The Fe—O distance is 1.921 (4) Å. The out-of-plane displacement and the Fe—N bond lengths indicate that the Fe atom is in a high-spin state.

Comment

The structures of five mononuclear high-spin pentacoordinate oxygen-ligated iron complexes of the type [$Fe^{III}(Por)(X)$] (where Por = tetraphenylporphinato, TPP, or tetrakis(*p*-methoxyphenyl)porphinato, t_p-MePP, and X = OCH_3, $OCOCH_3$, $OSOC_6H_5$, OSO_3H or OSO_2CH_3) have been determined previously (Lecomte, Chadwick, Coppens & Stevens, 1983; Oumous, Lecomte, Protas, Cocolios & Guilard, 1984; Cocolios, Lagrange, Guilard, Oumous & Lecomte, 1984; Scheidt, Lee & Finnegan, 1988; Li *et al.*, 1987). We report here the molecular stereochemistry of [$Fe^{III}(TPP)(OCOCF_3)$], (I), along with a structural comparison with related complexes.



(I)

Fig. 1 presents an *ORTEP* (Johnson, 1965) view of the molecule along with the numbering scheme employed for the non-H atoms. The packing diagram given in Fig. 2 shows that the molecules of the compound interact in pairs in the lattice. The coordination-group parameters for [$Fe^{III}(TPP)(OCOCF_3)$] are presented in Table 3 and

Acta Crystallographica Section C
ISSN 0108-2701 ©1995