Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
V1	0.56793 (8)	0.80814 (3)	0.01302 (8)	0.0177 (2)
O1	0.4892 (3)	0.70755 (14)	0.1799 (3)	0.0231 (4)
O2	0.4410 (5)	0.9007 (2)	0.0830 (5)	0.0389 (6)
O3	0.8367 (4)	0.8252 (2)	0.1074 (4)	0.0316 (5)
N1	0.8699 (4)	0.4182 (2)	0.0292 (5)	0.0228 (5)
C1	1.0005 (5)	0.4211 (2)	−0.1645 (6)	0.0271 (6)
C2	0.8003 (5)	0.5155 (2)	0.0843 (6)	0.0248 (6)

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

V1—O2	1.600 (3)	N1—C1	1.473 (4)
V1—O3	1.629 (3)	N1—C2	1.476 (4)
V1—O1^{i}	1.801 (3)	C1—C2^{ii}	1.492 (4)
V1—O1	1.803 (3)		
O2—V1—O3	108.5 (2)	O1^{i}—V1—O1	112.6 (1)
O2—V1—O1^{i}	108.1 (2)	V1^{iii}—O1—V1	125.0 (1)
O3—V1—O1^{i}	111.1 (2)	C1—N1—C2	110.7 (2)
O2—V1—O1	107.7 (2)	N1—C1—C2^{ii}	110.2 (3)
O3—V1—O1	108.7 (2)	N1—C2—C1^{ii}	110.5 (3)
C1—N1—C2···C1^{ii}	−57.6 (4)	C2—C1^{ii}—N1^{ii}—C2^{ii}	−57.4 (4)
N1—C2—C1^{ii}—N1^{ii}	57.3 (4)	C1^{ii}—N1^{ii}—C2^{ii}—C1	57.6 (4)

Symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $2-x, 1-y, -z$; (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
N1—H1···O1^{i}	2.04 (4)	2.85 (4)	170 (4)
N1—H2···O3^{ii}	1.88 (4)	2.70 (4)	168 (4)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

H atoms were refined isotropically, resulting in N—H bond lengths in the range 0.82–0.84 Å and C—H bond lengths in the range 0.92–0.96 Å. The values of U_{iso} for the H atoms lie in the range 0.019–0.042 Å².

Data reduction: *XP*21 (Pavelčík, unpublished program). Program(s) used to solve structure: *XFPS* (Pavelčík, Sivý, Rizzoli & Andreetti, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: BK1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Zirconocene Complex, [{η^5-C_5H_4-$C(CH_2)_5(CH_2)_2CH(CH_3)_2$}$_2ZrCl_2$]

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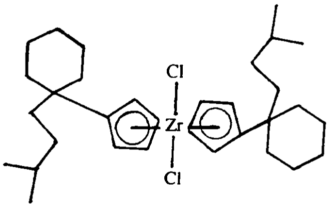
Abstract

The title compound, dichlorobis{η^5-[1-(3-methylbutyl)-cyclohex-1-yl]cyclopentadienyl}zirconium(IV), [$ZrCl_2(C_{16}H_{25})_2$], has a pseudo-tetrahedral bent-metallocene structure in which the substituted cyclopentadienyl rings are asymmetrically bonded to the central Zr atom, due primarily to the interaction between the large substituents and the Cl atoms. The molecule has local C_2 symmetry with the substituents positioned in a *trans* arrangement and directed towards the lateral sectors of the bent-metallocene unit.

Comment

Studies on variations of the Group 4 metallocene structures (Erker *et al.*, 1989) are a topic of great interest, primarily because of their unprecedented behaviour as catalyst precursors of homogeneous Ziegler–Natta polymerization systems (Sinn, Kaminsky, Vollmer & Woldt, 1980; Sinn & Kaminsky, 1980). The addition of stereochemistry-controlling substituents to the cyclopentadienyl (Cp) rings of zirconocene catalyst precursors influences considerably their α-olefin-polymerization activity (Kaminsky, 1986; Kaminsky, Engehausen, Zoumis, Spaleck & Rohrmann, 1992; Chien & Razavi, 1988; Tian & Huang, 1994), their molecular weight and their specific stereoselectivity (Erker *et al.*, 1991). In this paper, we present the structural study of a new substituted zirconocene, dichlorobis{η^5-[1-(3-methylbutyl)cyclohex-1-yl]cyclopentadienyl}zirconium(IV), (I).



(I)

The molecular structure of the title compound has bent C_2-symmetric metallocene geometry, with the zirconium centre pseudo-tetrahedrally coordinated by two

$[\eta^5\text{-}C_5H_4\text{-}C(CH_2)_5(CH_2)_2CH(CH_3)_2]$ and two Cl ligands, where each cyclopentadienyl ring is considered as occupying a single coordination site. Both cyclopentadienyl rings are planar, with a maximum displacement of the C atoms from the least-squares planes of 0.017 (7) Å.

The Cl—Zr—Cl angle is 93.7 (1)° and the Zr—Cl distance is 2.460 (1) Å. These values are normal and comparable with published data for many $[(R\mathrm{Cp})_2ZrCl_2]$ complexes bearing, for example, bulky *tert*-alkyl substituents on the cyclopentadienyl rings (Howie, Mcquillan, Thompson & Lock, 1986; Erker *et al.*, 1989). The substituted cyclopentadienyl ring systems are in a staggered orientation. The dihedral angle between the two cyclopentadienyl rings is 52.4 (5)°. The $C(CH_2)_5(CH_2)_2CH(CH_3)_2$ side chains, which point away from each other, are positioned in a *trans* arrangement and directed towards the lateral sectors of the bent-metallocene unit. This conformational arrangement is similar to that found in many $[(\textit{tert}\text{-alkyl-Cp})_2ZrCl_2]$ complexes (Erker *et al.*, 1989; Howie, Mcquillan, Thompson & Lock, 1986). The substituent torsion angle, defined as θ_s [C(1)—*CEN*—*CEN*$^{\rm i}$—C(1$^{\rm i}$), where *CEN* and *CEN*$^{\rm i}$ are the centroids of the cyclopentadieyl ring and its symmetry-generated partner, respectively], is −178.8 (1)°, close to that found for the above mentioned $[(\textit{tert}\text{-alkyl-Cp})_2ZrCl_2]$ complexes. The pentamethylene substituents bonded to atoms C(1) and C(1$^{\rm i}$) are directed towards the lateral sectors of the bent metallocene, while the C(1)—C(7) vector points to the 'close' side of the bent-metallocene wedge. This is in contrast to what was found in bis(1-methylcyclohexyl)-zirconocene dichloride (Erker *et al.*, 1989).

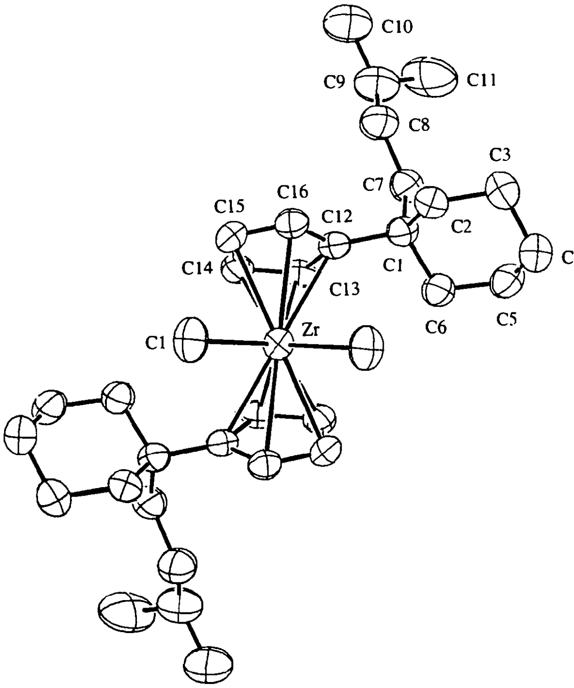


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Attributed primarily to the interaction of the large substituent with the Cl atom, the cyclopentadienyl ring is asymmetrically bonded to Zr and tilted in such a way that the Zr—C(12) bond is the longest, resulting in a 'Zr-slippage' structure (Ogasa *et al.*, 1991; Gelmini, Puddephatt & Vittal, 1993). The difference between the longest and the shortest bond from the Zr atom to C atoms in the same cyclopentadienyl ring is 0.131 (4) Å, which is much larger than that observed in $[Cp_2ZrCl_2]$ (0.03 Å; Prout *et al.*, 1974).

Experimental

The synthesis of the title compound was carried out by reaction of 6,6-pentamethylenefulvene ($C_{11}H_{14}$) with organolithium followed by treatment with zirconium tetrachloride in benzene solution for 1 h at room temperature in a glass vessel, using standard Schlenk techniques. Recrystallization was from toluene/oil ether (333–363 K).

Crystal data

$[ZrCl_2(C_{16}H_{25})_2]$
$M_r = 596.87$
Monoclinic
$C2/c$
$a = 32.549\ (8)$ Å
$b = 6.604\ (1)$ Å
$c = 14.933\ (5)$ Å
$\beta = 95.21\ (2)°$
$V = 3196\ (1)$ Å^3
$Z = 4$
$D_x = 1.24$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2.7\text{–}10.5°$
$\mu = 0.52$ mm^{-1}
$T = 293$ K
Flat slice
0.61 × 0.24 × 0.12 mm
Colourless

Data collection

Nicolet *R*3*m*/*E* diffractometer
ω scans (5.86° min^{-1}, width 1.4°)
Absorption correction: refined from ΔF
$T_{\rm min} = 0.87$, $T_{\rm max} = 0.91$
2807 measured reflections
2807 independent reflections

1988 observed reflections $[I > 3\sigma(I)]$
$\theta_{\rm max} = 25.0°$
$h = -38 \rightarrow 38$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 17$
2 standard reflections monitored every 98 reflections intensity decay: <2.5%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.044$
$S = 1.23$
1988 reflections
159 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.0005(F_o)^2]$
$(\Delta/\sigma)_{\rm max} = 0.032$
$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
Zr	0	0.1003 (1)	1/4	0.043 (1)
Cl	−0.0256 (1)	−0.1544 (1)	0.3514 (1)	0.061 (1)
C(1)	0.1066 (1)	0.2467 (5)	0.1953 (2)	0.051 (1)
C(2)	0.1287 (1)	0.0414 (6)	0.1871 (2)	0.060 (1)
C(3)	0.1584 (1)	0.0391 (7)	0.1137 (3)	0.072 (2)
C(4)	0.1356 (1)	0.0923 (8)	0.0231 (3)	0.082 (2)
C(5)	0.1140 (1)	0.2959 (8)	0.0266 (3)	0.075 (2)
C(6)	0.0854 (1)	0.3049 (6)	0.1018 (2)	0.058 (1)
C(7)	0.1378 (1)	0.4127 (6)	0.2281 (2)	0.063 (1)
C(8)	0.1642 (1)	0.3689 (7)	0.3155 (3)	0.078 (2)
C(9)	0.1911 (2)	0.5298 (9)	0.3543 (3)	0.099 (2)
C(10)	0.2149 (2)	0.4685 (11)	0.4405 (3)	0.125 (3)
C(11)	0.2171 (2)	0.6368 (9)	0.2951 (4)	0.127 (3)
C(12)	0.0753 (1)	0.2354 (5)	0.2649 (2)	0.046 (1)
C(13)	0.0482 (1)	0.3919 (5)	0.2849 (2)	0.050 (1)
C(14)	0.0297 (1)	0.3438 (6)	0.3634 (2)	0.056 (1)
C(15)	0.0448 (1)	0.1553 (6)	0.3934 (2)	0.058 (1)
C(16)	0.0718 (1)	0.0856 (5)	0.3317 (2)	0.052 (1)

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

Zr—Cl	2.460 (1)	Zr—*CEN*†	2.224 (1)
Zr—C(12)	2.599 (3)	Zr—C(13)	2.508 (3)
Zr—C(14)	2.468 (4)	Zr—C(15)	2.506 (3)
Zr—C(16)	2.539 (3)	C(1)—C(2)	1.544 (5)
C(1)—C(6)	1.549 (6)	C(1)—C(7)	1.542 (5)
C(1)—C(12)	1.521 (5)	C(2)—C(3)	1.526 (6)
C(3)—C(4)	1.524 (6)	C(4)—C(5)	1.520 (7)
C(5)—C(6)	1.523 (5)	C(7)—C(8)	1.525 (5)
C(8)—C(9)	1.463 (7)	C(9)—C(10)	1.496 (7)
C(9)—C(11)	1.461 (8)	C(12)—C(13)	1.410 (5)
C(12)—C(16)	1.417 (5)	C(13)—C(14)	1.402 (5)
C(14)—C(15)	1.397 (5)	C(15)—C(16)	1.406 (5)
CEN—Zr—Cl	105.3 (1)	*CEN*—Zr—Cl^i	108.3 (1)
Cl—Zr—Cl^i	93.7 (1)	*CEN*—Zr—*CEN*^{i}	130.1 (1)
C(12)—Zr—C(12^i)	139.9 (1)	C(16)—Zr—C(12^i)	151.0 (1)
C(1)—C(12)—C(13)	125.5 (3)	C(1)—C(12)—C(16)	128.1 (3)
C(13)—C(12)—C(16)	105.7 (3)	C(12)—C(13)—C(14)	109.6 (3)
C(13)—C(14)—C(15)	107.7 (3)	C(14)—C(15)—C(16)	107.8 (3)
C(15)—C(16)—C(12)	109.1 (3)	C(12)—C(1)—C(7)	106.3 (3)
C(12)—C(1)—C(6)	110.9 (3)	C(12)—C(1)—C(2)	110.9 (3)
C(2)—C(1)—C(6)	108.5 (3)	C(2)—C(1)—C(7)	110.6 (3)
C(6)—C(1)—C(7)	109.6 (3)	C(1)—C(2)—C(3)	113.3 (3)
C(2)—C(3)—C(4)	110.2 (3)	C(4)—C(5)—C(6)	112.1 (4)
C(5)—C(6)—C(1)	113.8 (3)	C(1)—C(7)—C(8)	116.1 (3)
C(7)—C(8)—C(9)	118.2 (4)	C(8)—C(9)—C(10)	112.9 (5)
C(8)—C(9)—C(11)	118.1 (4)	C(10)—C(9)—C(11)	111.6 (4)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

† *CEN* is the centroid of the cyclopentadienyl ring.

The structure was solved by heavy-atom methods and refined by block-diagonal least squares with anisotropic displacement parameters for all non-H atoms. H atoms were introduced at calculated positions and fixed with isotropic displacement parameters (U_{iso} = 0.06 Å²) in the final cycles of refinement.

Data collection and cell refinement: *P*3 *Program* (Nicolet XRD Corporation, 1985). Data reduction, structure solution and refinement, molecular graphics and preparation of material for publication: *SHELXTL Users Manual* (Sheldrick, 1985).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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catena-{[$HgCl_2$([18]aneS_2O_4)]$HgCl_2$} at 150 K: a Redetermination and Reinterpretation

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Abstract

The structure of the title compound {[$HgCl_2$([18]aneS_2O_4)]$HgCl_2$}$_n$ ([18]aneS_2O_4 = 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane), [$Hg_2Cl_4(C_{12}H_{24}O_4S_2)$], has been redetermined and reinterpreted as a one-dimensional polymeric thread comprising linked Hg_4Cl_4

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