metal-organic compounds

Dibromido[bis(η^5-cyclopentadienyl)-dimethylsilane]zirconium(IV)

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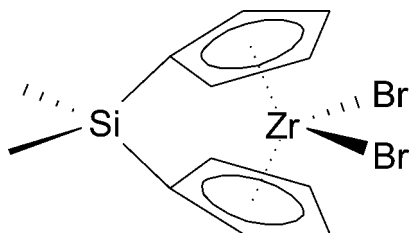Correspondence e-mail: milan.erben@upce.cz

The title molecule, [ZrBr$_2$(C$_{12}$H$_{14}$Si)], possesses a crystallographically imposed twofold rotational symmetry with the rotation axis passing through the Zr and Si atoms. The Zr^{IV} centre is in a distorted tetrahedral environment defined by two Cp rings of chelating organic ligands and two Br anions. Two five-membered rings form a dihedral angle of 59.7 (2)°. Unequal Zr—C bonds [2.471 (3)–2.556 (3) Å] in the molecule indicate that the interaction of the central metal with the [(C$_5$H$_4$)$_2$SiMe$_2$]$^{2-}$ ligand contains noticeable η^3-allyl and η^2-olefin contributions.

Related literature

For related ansa-zirconocenes, see, for example: Bajgur *et al.* (1985), Borrelli *et al.* (2002).

Experimental

Crystal data

[ZrBr$_2$(C$_{12}$H$_{14}$Si)]	b = 10.0990 (2) Å
M_r = 437.36	c = 10.9770 (3) Å
Monoclinic, $C2/c$	β = 112.2540 (12)°
a = 13.6160 (4) Å	V = 1396.99 (6) Å^3
Z = 4	T = 120 (2) K
Mo $K\alpha$ radiation	0.40 × 0.30 × 0.22 mm
μ = 6.57 mm^{-1}	

Data collection

Nonius KappaCCD area-detector diffractometer	9698 measured reflections
Absorption correction: Gaussian (Coppens *et al.*, 1970)	1602 independent reflections
T_{min} = 0.137, T_{max} = 0.271	1560 reflections with $I > 2\sigma(I)$
	R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024	76 parameters
$wR(F^2)$ = 0.063	H-atom parameters constrained
S = 1.14	$\Delta\rho_{max}$ = 0.69 e Å^{-3}
1602 reflections	$\Delta\rho_{min}$ = −1.07 e Å^{-3}

Table 1
Selected geometric parameters (Å°,).

Zr1—Cg1	2.199 (1)	C6—Si1—C6^i	116.0 (1)
Zr1—Br1	2.6007 (4)	C1—Si1—C1^i	93.2 (1)
Cg1—Zr1—Cg1^i	125.96 (5)	Br1—Zr1—Br1^i	98.39 (1)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$. Cg1 is the centroid of atoms C1–C5.

Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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supporting information

Dibromido[bis(η^5-cyclopentadienyl)dimethylsilane]zirconium(IV)

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S1. Comment

Metallocene complexes of Group 4 are intensively investigated as very efficient and selective olefin polymerization and co-polymerization catalysts (Borrelli *et al.*, 2002). The most used strategy for the modification of catalytic properties of these metallocenes is the substitution at the cyclopentadienyl rings. Incorporation of an interannular bridge connecting both cyclopentadienyl rings in the molecule of metallocene leads to a broad class of complexes known as ansa-metallocenes. As part of an investigation of the influence of ring substitution on the properties of cyclopentadienyl complexes, the title compound, (I), was prepared, spectroscopically characterized and its structure determined

  A perspective view of molecular structure of (I) is shown in Figure 1 with appropriate atom labeling scheme, selected bond distances and angles are summarized in Table 1. In the molecule of (I) the Zr atom is pseudotetrahedrally coordinated by two η^5-bonded Cp rings and two Br atoms with geometry constrained by crystallographic twofold rotation axis, which bisects Br1—Zr—Br1a angle and passes through the metal and Si atom. The molecular parameters are comparable to those reported for [ZrCl$_2$(η^5-C$_5$H$_4$)$_2$SiMe$_2$] (Bajgur *et al.*, 1985). On the inspection of parameters associated with Cp rings, the deviation from the ideal η^5-bonding fashion could be observed. The C3—C4 bond distance of 1.400 (6) Å is shorter than the remaining C—C bonds (average of 1.42 Å). Similarly Zr1—C3 and Zr1—C4 bonds are longer [2.556 (3) Å and 2.552 (4) Å, respectively] than remaining metal-carbon bonds (average of 2.475 Å). These facts indicate the presence of η^3-allyl and η^2-olefin bonding fashion of Cp ring rather than η^5-cyclopentadienyl bonding pattern.

S2. Experimental

Compound (I) was prepared by bromination of analogous chloride derivative using boron tribromide. To the starting complex [ZrCl$_2$(η^5-C$_5$H$_4$)$_2$SiMe$_2$] (0.2 g; 0.57 mol) in 20 ml of dichloromethane 0.04 ml (0.42 mmol) of BBr$_3$ was added. The color of the reaction mixture immediatelly turned to green and it was stirred for additional 2 h at 293 K. The solvent was evaporated in vacuum, solid residue was washed with hexane (2x5 ml) and vacuum-dried. Sublimation of crude product at 10^{-3} Pa and 475 K gave 0.105 g (42%) of (I). Crystals of (I) suitable for X-ray diffraction measurements were grown during slow evaporation of chloroform solution at 273 K.

S3. Refinement

All H atoms were positioned geometrically and refined as riding on their parent C atoms, with C—H = 0.93 Å, U_{iso}(H) = 1.2U$_{e.g}$(C) and C—H = 0.96 Å, U_{iso}(H) = 1.5U$_{e.g}$(C) for cyclopentadienyl and methyl H atoms, respectively.
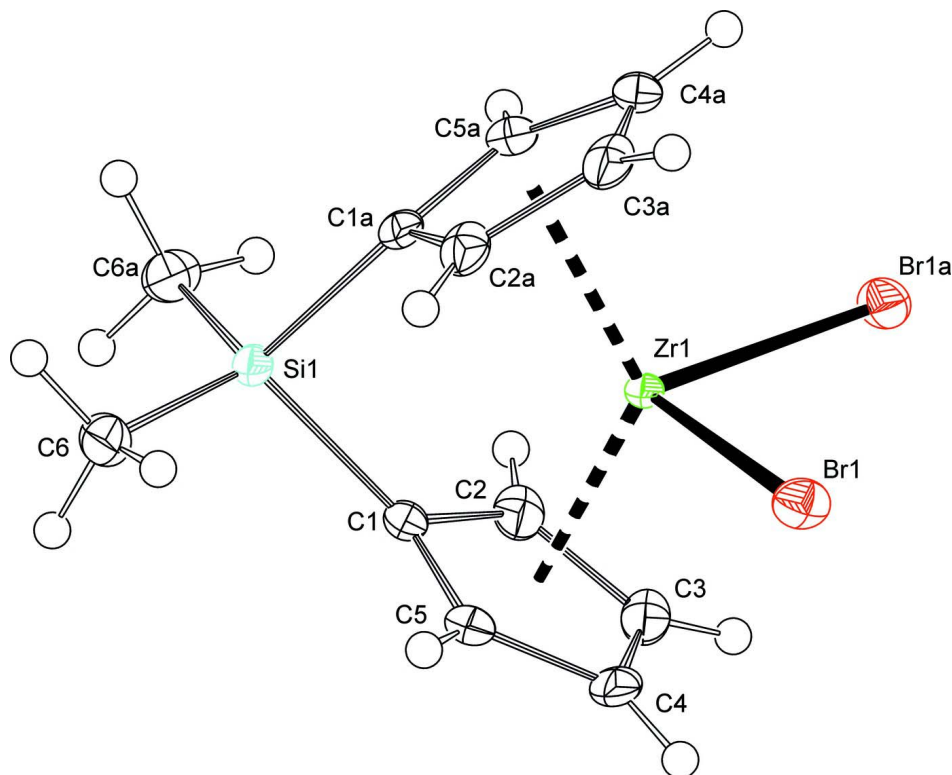
Figure 1

Perspective view of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms) [symmetry code: (*a*) -*x*, *y*, $\frac{1}{2}$-*z*.]

Dibromido[bis(*η*⁵-cyclopentadienyl)dimethylsilane]zirconium(IV)

Crystal data

[ZrBr$_2$(C$_{12}$H$_{14}$Si)]	$F(000) = 840$
$M_r = 437.36$	$D_x = 2.079$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 6471 reflections
$a = 13.6160$ (4) Å	$\theta = 1–27.5°$
$b = 10.0990$ (2) Å	$\mu = 6.57$ mm^{-1}
$c = 10.9770$ (3) Å	$T = 120$ K
$\beta = 112.2540$ (12)°	Prism, yellow
$V = 1396.99$ (6) Å^3	$0.4 \times 0.3 \times 0.22$ mm
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	9698 measured reflections
Radiation source: fine-focus sealed tube	1602 independent reflections
Graphite monochromator	1560 reflections with $I > 2\sigma(I)$
Detector resolution: 9.091 pixels mm^{-1}	$R_{int} = 0.047$
φ and ω scans to fill the Ewald sphere	$\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$
Absorption correction: gaussian (Coppens et al., 1970)	$h = -17 \rightarrow 17$
	$k = -13 \rightarrow 13$
$T_{min} = 0.137$, $T_{max} = 0.271$	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.024$	H-atom parameters constrained
$wR(F^2) = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 3.2435P]$
$S = 1.14$	where $P = (F_o^2 + 2F_c^2)/3$
1602 reflections	$(\Delta/\sigma)_{max} < 0.001$
76 parameters	$\Delta\rho_{max} = 0.69$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -1.07$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: *SHELXL97* (Sheldrick, 1997), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0044 (3)

Special details

Experimental. Spectroscopic analysis: ^{1}H NMR (CDCl$_3$, δ, p.p.m.): 7.15 (m, 4H), 5.97 (m, 4H), 0.73 (s, 6H). ^{13}C NMR (CDCl$_3$, δ, p.p.m.): -5.2, 1, 114.3, 115.8, 128.9. IR (KBr disc, cm^{-1}): 3115 (*m*), 3099 (*m*), 3074 (*m*), 2964 (*m*), 2958 (*m*), 1448 (*m*), 1409 (w), 1400 (*s*), 1370 (*s*), 1362 (*m*), 1324 (*m*), 1314 (w), 1260 (*s*), 1200 (w), 1179 (*s*), 1168 (*s*), 1069 (*s*), 1048 (*s*), 1020 (*s*), 942 (*m*), 902 (*s*), 870 (*s*), 870 (*s*), 813 (*s*), 680 (*s*), 633 (*s*), 555 (*m*), 502 (*m*), 454 (*s*), 420 (*s*), 384 (*m*), 347 (*s*); UV-Vis (CH$_2$Cl$_2$, maxima at nm): 470, 377, 313, 233. Elemental analysis, calculated for C$_{12}$H$_{14}$Br$_2$SiZr: C 32.96, H 3.23; found: C 32.61, H 3.14%.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Zr1	0.0000	0.31648 (3)	0.2500	0.01164 (12)
Br1	0.155827 (19)	0.48477 (3)	0.33572 (2)	0.02090 (12)
Si1	0.0000	−0.01625 (9)	0.2500	0.0160 (2)
C1	0.0077 (2)	0.1116 (2)	0.1295 (2)	0.0170 (5)
C2	−0.0792 (2)	0.1870 (3)	0.0443 (3)	0.0206 (5)
H2	−0.1504	0.1647	0.0193	0.025*
C3	−0.0400 (3)	0.3017 (3)	0.0033 (3)	0.0250 (6)
H3	−0.0807	0.3658	−0.0547	0.030*
C4	0.0707 (3)	0.3014 (3)	0.0658 (3)	0.0247 (6)
H4	0.1166	0.3654	0.0567	0.030*
C5	0.1003 (2)	0.1861 (3)	0.1454 (3)	0.0207 (5)
H5	0.1693	0.1630	0.1993	0.025*
C6	0.1245 (2)	−0.1135 (3)	0.3168 (3)	0.0247 (6)
H6A	0.1191	−0.1775	0.3787	0.037*
H6B	0.1830	−0.0551	0.3603	0.037*
H6C	0.1359	−0.1583	0.2462	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.01466 (17)	0.01152 (18)	0.01051 (17)	0.000	0.00678 (12)	0.000
Br1	0.01687 (16)	0.02362 (18)	0.02273 (17)	−0.00544 (9)	0.00811 (11)	−0.00413 (9)
Si1	0.0237 (5)	0.0120 (4)	0.0156 (5)	0.000	0.0112 (4)	0.000
C1	0.0261 (12)	0.0145 (11)	0.0147 (11)	0.0005 (10)	0.0125 (9)	−0.0021 (9)
C2	0.0282 (13)	0.0187 (13)	0.0134 (11)	−0.0003 (10)	0.0062 (10)	−0.0028 (9)
C3	0.0467 (17)	0.0181 (13)	0.0122 (11)	0.0029 (12)	0.0134 (11)	0.0003 (10)
C4	0.0435 (16)	0.0189 (13)	0.0224 (13)	−0.0035 (12)	0.0245 (12)	−0.0017 (10)
C5	0.0272 (13)	0.0193 (13)	0.0227 (13)	0.0015 (10)	0.0176 (11)	−0.0012 (10)
C6	0.0321 (14)	0.0228 (14)	0.0220 (13)	0.0080 (12)	0.0135 (11)	0.0048 (11)

Geometric parameters (Å, º)

Zr1—C5[i]	2.471 (3)	Si1—C1[i]	1.880 (3)
Zr1—C5	2.471 (3)	Si1—C1	1.880 (3)
Zr1—C2[i]	2.476 (3)	C1—C2	1.420 (4)
Zr1—C2	2.476 (3)	C1—C5	1.422 (4)
Zr1—C1	2.480 (2)	C2—C3	1.418 (4)
Zr1—C1[i]	2.480 (2)	C2—H2	0.9300
Zr1—C4[i]	2.552 (3)	C3—C4	1.400 (4)
Zr1—C4	2.552 (3)	C3—H3	0.9300
Zr1—C3	2.556 (3)	C4—C5	1.420 (4)
Zr1—C3[i]	2.556 (3)	C4—H4	0.9300
Zr1—Br1[i]	2.6007 (3)	C5—H5	0.9300
Zr1—Br1	2.6007 (3)	C6—H6A	0.9600
Si1—C6[i]	1.853 (3)	C6—H6B	0.9600
Si1—C6	1.853 (3)	C6—H6C	0.9600
C5[i]—Zr1—C5	115.60 (12)	C3[i]—Zr1—Br1[i]	103.82 (7)
C5[i]—Zr1—C2[i]	54.64 (9)	C5[i]—Zr1—Br1	134.35 (7)
C5—Zr1—C2[i]	90.90 (9)	C5—Zr1—Br1	89.86 (6)
C5[i]—Zr1—C2	90.90 (9)	C2[i]—Zr1—Br1	90.07 (6)
C5—Zr1—C2	54.64 (9)	C2—Zr1—Br1	133.57 (7)
C2[i]—Zr1—C2	116.22 (12)	C1—Zr1—Br1	123.01 (6)
C5[i]—Zr1—C1	86.89 (8)	C1[i]—Zr1—Br1	123.08 (6)
C5—Zr1—C1	33.37 (8)	C4[i]—Zr1—Br1	104.65 (7)
C2[i]—Zr1—C1	87.36 (9)	C4—Zr1—Br1	79.92 (7)
C2—Zr1—C1	33.31 (9)	C3—Zr1—Br1	103.82 (7)
C5[i]—Zr1—C1[i]	33.37 (8)	C3[i]—Zr1—Br1	80.64 (7)
C5—Zr1—C1[i]	86.89 (8)	Br1[i]—Zr1—Br1	98.387 (17)
C2[i]—Zr1—C1[i]	33.31 (9)	C6[i]—Si1—C6	116.0 (2)
C2—Zr1—C1[i]	87.36 (9)	C6[i]—Si1—C1[i]	110.88 (12)
C1—Zr1—C1[i]	66.87 (11)	C6—Si1—C1[i]	111.83 (12)
C5[i]—Zr1—C4[i]	32.79 (9)	C6[i]—Si1—C1	111.83 (12)
C5—Zr1—C4[i]	141.00 (9)	C6—Si1—C1	110.87 (12)
C2[i]—Zr1—C4[i]	53.88 (9)	C1[i]—Si1—C1	93.26 (15)

C2—Zr1—C4ⁱ	121.77 (9)	C2—C1—C5	106.1 (2)
C1—Zr1—C4ⁱ	118.55 (9)	C2—C1—Si1	125.24 (19)
C1ⁱ—Zr1—C4ⁱ	54.73 (8)	C5—C1—Si1	124.1 (2)
C5ⁱ—Zr1—C4	141.00 (9)	C2—C1—Zr1	73.19 (14)
C5—Zr1—C4	32.80 (9)	C5—C1—Zr1	72.99 (14)
C2ⁱ—Zr1—C4	121.77 (9)	Si1—C1—Zr1	99.94 (10)
C2—Zr1—C4	53.88 (9)	C3—C2—C1	109.1 (2)
C1—Zr1—C4	54.73 (8)	C3—C2—Zr1	76.77 (15)
C1ⁱ—Zr1—C4	118.55 (9)	C1—C2—Zr1	73.51 (14)
C4ⁱ—Zr1—C4	173.17 (13)	C3—C2—H2	125.5
C5ⁱ—Zr1—C3	121.83 (10)	C1—C2—H2	125.5
C5—Zr1—C3	53.87 (9)	Zr1—C2—H2	116.2
C2ⁱ—Zr1—C3	141.26 (9)	C4—C3—C2	107.9 (2)
C2—Zr1—C3	32.69 (9)	C4—C3—Zr1	73.94 (15)
C1—Zr1—C3	54.63 (8)	C2—C3—Zr1	70.54 (15)
C1ⁱ—Zr1—C3	118.78 (9)	C4—C3—H3	126.0
C4ⁱ—Zr1—C3	147.45 (10)	C2—C3—H3	126.0
C4—Zr1—C3	31.81 (10)	Zr1—C3—H3	121.2
C5ⁱ—Zr1—C3ⁱ	53.87 (9)	C3—C4—C5	107.8 (2)
C5—Zr1—C3ⁱ	121.83 (10)	C3—C4—Zr1	74.25 (15)
C2ⁱ—Zr1—C3ⁱ	32.69 (9)	C5—C4—Zr1	70.48 (14)
C2—Zr1—C3ⁱ	141.25 (9)	C3—C4—H4	126.1
C1—Zr1—C3ⁱ	118.78 (9)	C5—C4—H4	126.1
C1ⁱ—Zr1—C3ⁱ	54.63 (8)	Zr1—C4—H4	120.9
C4ⁱ—Zr1—C3ⁱ	31.81 (10)	C4—C5—C1	109.0 (2)
C4—Zr1—C3ⁱ	147.45 (10)	C4—C5—Zr1	76.72 (15)
C3—Zr1—C3ⁱ	173.31 (13)	C1—C5—Zr1	73.64 (14)
C5ⁱ—Zr1—Br1ⁱ	89.86 (6)	C4—C5—H5	125.5
C5—Zr1—Br1ⁱ	134.35 (7)	C1—C5—H5	125.5
C2ⁱ—Zr1—Br1ⁱ	133.57 (7)	Zr1—C5—H5	116.1
C2—Zr1—Br1ⁱ	90.07 (6)	Si1—C6—H6A	109.5
C1—Zr1—Br1ⁱ	123.08 (6)	Si1—C6—H6B	109.5
C1ⁱ—Zr1—Br1ⁱ	123.01 (6)	H6A—C6—H6B	109.5
C4ⁱ—Zr1—Br1ⁱ	79.92 (7)	Si1—C6—H6C	109.5
C4—Zr1—Br1ⁱ	104.65 (7)	H6A—C6—H6C	109.5
C3—Zr1—Br1ⁱ	80.64 (7)	H6B—C6—H6C	109.5

Symmetry code: (i) −*x*, *y*, −*z*+1/2.