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 Tris(η^5 -cyclopentadienyl)hafnium(III)

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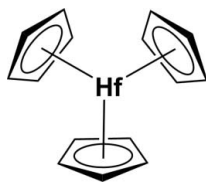
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å; R factor = 0.034; wR factor = 0.076; data-to-parameter ratio = 13.4.

In the crystal structure of the title compound, $[\text{Hf}(\text{C}_5\text{H}_5)_3]$, three cyclopentadienyl ligands surround the Hf^{III} atom in a trigonal-planar geometry. The molecule lies on a sixfold inversion axis.

Related literature

Isotypic $(\eta^5\text{-C}_5\text{H}_5)_3\text{Zr}$ was described by Lukens & Andersen (1995). For $(\eta^5\text{-C}_5\text{H}_5)_3M$, $M = \text{Y}$: see Adam *et al.* (1991); $M = \text{Nd}$: see Eggers *et al.* (1992a); $M = \text{Sm}$: see Wong *et al.* (1969), Bel'skii *et al.* (1991), Eggers *et al.* (1992b); $M = \text{Er}$, Tm : see Eggers *et al.* (1986); $M = \text{Yb}$: see Eggers *et al.* (1987); $M = \text{Ce}$, Dy , Ho : see Baisch *et al.* (2006). Unit-cell dimensions of $(\eta^5\text{-C}_5\text{H}_5)_3M$ ($M = \text{Pr}$, Pm , Sm , Gd , Tb , Tm , Cm , Bk , Cf) were determined by Laubereau & Burns (1970a,b).



Experimental

Crystal data

$[\text{Hf}(\text{C}_5\text{H}_5)_3]$	$Z = 2$
$M_r = 373.76$	Mo $K\alpha$ radiation
Hexagonal, $P6_3/m$	$\mu = 9.16 \text{ mm}^{-1}$
$a = 7.9772$ (4) Å	$T = 150$ K
$c = 10.2975$ (6) Å	$0.30 \times 0.20 \times 0.15$ mm
$V = 567.50$ (5) Å ³	

Data collection

Stoe IPDS II diffractometer	7314 measured reflections
Absorption correction: numerical (<i>X-SHAPE</i> and <i>X-RED32</i> ; Stoe & Cie, 2005)	362 independent reflections
$T_{\text{min}} = 0.150$, $T_{\text{max}} = 0.346$	333 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.097$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	27 parameters
$wR(F^2) = 0.076$	H-atom parameters constrained
$S = 1.22$	$\Delta\rho_{\text{max}} = 0.95 \text{ e \AA}^{-3}$
362 reflections	$\Delta\rho_{\text{min}} = -3.40 \text{ e \AA}^{-3}$

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP in SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5148).

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supporting information

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Tris(η^5 -cyclopentadienyl)hafnium(III)

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S1. Comment

In the reaction of (η^5 -C₅H₅)₂Hf[—C(SiMe₃)=C(C≡CSiMe₃)—C(SiMe₃)=C(C≡CSiMe₃)—] with (*i*-Bu)₂AlH single crystals of the title compound as lone product in very low yield were isolated. Isostructural compounds are known for *M* = Zr (Lukens *et al.*, 1995), *M* = Y (Adam *et al.*, 1991), *M* = Nd (Eggers *et al.*, 1992*a*), *M* = Sm (Wong *et al.*, 1969; Bel'skii *et al.*, 1991; Eggers *et al.*, 1992*b*), *M* = Er, Tm (Eggers *et al.*, 1986), *M* = Yb (Eggers *et al.*, 1987), *M* = Ce, Dy, Ho (Baisch *et al.*, 2006). (η^5 -C₅H₅)₃Hf crystallizes in the hexagonal space group *P*6₃/*m* with unit-cell dimensions isomorphous with the Zr analogue (Lukens *et al.*, 1995). The Hf(III) center is surrounded by three η^5 -coordinated cyclopentadienyl ligands in a trigonal planar geometry. The Hf—C distances are with 2.547 (6) and 2.575 (6) Å in the expected range.

S2. Experimental

An amount of 0.460 g (0.66 mmol) of the five membered metallacycle (η^5 -C₅H₅)₂Hf[—C(SiMe₃)=C(C≡CSiMe₃)—C(SiMe₃)=C(C≡CSiMe₃)—] was dissolved in 20 ml of *n*-hexane under Ar, and 2.6 ml (2.6 mmol) of a 1.0 *M* solution of (*i*-Bu)₂AlH in cyclohexane was added to the obtained yellow solution. After one day the obtained red-brown solution was filtered and allowed to stand in argon atmosphere at -40 °C. After 6 month the light-yellow crystals had formed which were separated from the mother liquor by decanting, washed with cooled *n*-hexane, and dried in vacuum to give (η^5 -C₅H₅)₃Hf. Yield 9.3% (23 mg). *M.p.* 261–263 °C (dec. under Ar). *MS* (70 eV, *m/z*): 375 (*M*⁺), 310 (*M*⁺-C₅H₅).

S3. Refinement

H atoms were placed in idealized positions with *d*(C—H) = 0.95 Å and refined using a riding model with *U*_{iso}(H) fixed at 1.2 *U*_{eq}(C).

A numerical absorption correction was performed. Hence the largest peak of 0.95 (1.57 Å from Hf1) and the deepest hole of -3.40 e Å⁻³ (0.98 Å from Hf1) in the final difference Fourier map were obtained.

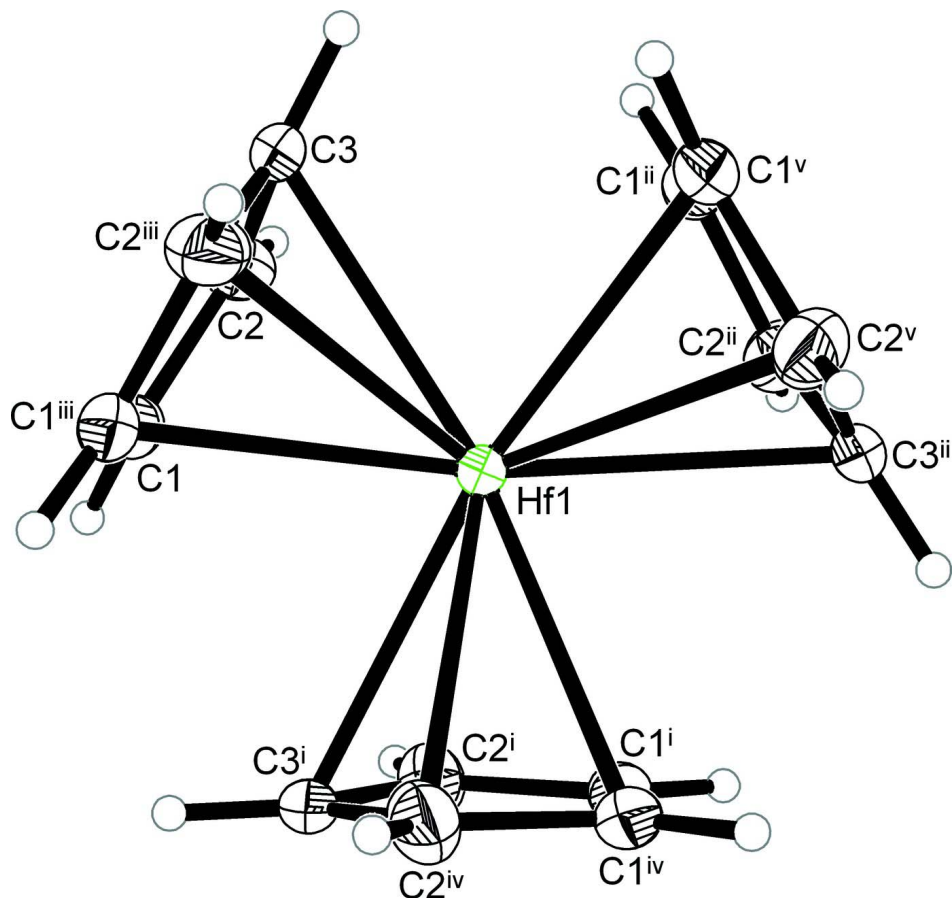


Figure 1

The molecular structure of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Tris(η^5 -cyclopentadienyl)hafnium(III)

Crystal data

[Hf(C₅H₅)₃]

$M_r = 373.76$

Hexagonal, $P6_3/m$

Hall symbol: -P 6c

$a = 7.9772$ (4) Å

$c = 10.2975$ (6) Å

$V = 567.50$ (5) Å³

$Z = 2$

$F(000) = 354$

$D_x = 2.187$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4609 reflections

$\theta = 1.9$ – 28.4°

$\mu = 9.16$ mm⁻¹

$T = 150$ K

Prism, yellow

$0.30 \times 0.20 \times 0.15$ mm

Data collection

Stoe IPDS II

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: numerical

(*X-SHAPE* and *X-RED32*; Stoe & Cie, 2005)

$T_{\min} = 0.150$, $T_{\max} = 0.346$

7314 measured reflections

362 independent reflections

333 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.097$
 $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 3.0^\circ$
 $h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.076$
 $S = 1.22$
 362 reflections
 27 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 5.6136P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.95 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -3.40 \text{ e } \text{\AA}^{-3}$

Special details

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Hf1	0.3333	0.6667	0.2500	0.0342 (3)
C1	0.4331 (9)	0.4179 (9)	0.1824 (6)	0.0236 (13)
H1	0.5434	0.4592	0.1283	0.028*
C2	0.2408 (10)	0.3460 (10)	0.1393 (7)	0.0300 (15)
H2	0.1992	0.3347	0.0517	0.036*
C3	0.1229 (14)	0.2944 (13)	0.2500	0.026 (2)
H3	-0.0143	0.2344	0.2500	0.032*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hf1	0.0126 (3)	0.0126 (3)	0.0772 (6)	0.00632 (15)	0.000	0.000
C1	0.022 (3)	0.019 (3)	0.031 (3)	0.011 (3)	0.003 (3)	-0.002 (3)
C2	0.024 (3)	0.027 (4)	0.035 (4)	0.010 (3)	-0.004 (3)	-0.001 (3)
C3	0.017 (4)	0.014 (4)	0.048 (6)	0.008 (4)	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Hf1—C2 ⁱ	2.549 (7)	Hf1—C1	2.576 (6)
Hf1—C2 ⁱⁱ	2.549 (7)	Hf1—C1 ⁱⁱ	2.576 (6)
Hf1—C2 ⁱⁱⁱ	2.549 (7)	C1—C1 ⁱⁱ	1.392 (12)
Hf1—C2 ^{iv}	2.549 (7)	C1—C2	1.414 (9)

Hf1—C2	2.549 (7)	C1—H1	0.9500
Hf1—C2 ^v	2.549 (7)	C2—C3	1.402 (9)
Hf1—C1 ⁱ	2.576 (6)	C2—H2	0.9500
Hf1—C1 ⁱⁱⁱ	2.576 (6)	C3—C2 ⁱⁱ	1.402 (9)
Hf1—C1 ^{iv}	2.576 (6)	C3—H3	0.9500
Hf1—C1 ^v	2.576 (6)		
C2 ⁱ —Hf1—C2 ⁱⁱ	101.55 (19)	C1 ⁱ —Hf1—C1 ^v	122.45 (4)
C2 ⁱ —Hf1—C2 ⁱⁱⁱ	53.1 (3)	C1 ⁱⁱⁱ —Hf1—C1 ^v	112.98 (12)
C2 ⁱⁱ —Hf1—C2 ⁱⁱⁱ	126.86 (8)	C1 ^{iv} —Hf1—C1 ^v	31.4 (3)
C2 ⁱ —Hf1—C2 ^{iv}	101.55 (19)	C2 ⁱ —Hf1—C1	152.1 (2)
C2 ⁱⁱ —Hf1—C2 ^{iv}	101.55 (19)	C2 ⁱⁱ —Hf1—C1	52.7 (2)
C2 ⁱⁱⁱ —Hf1—C2 ^{iv}	126.86 (8)	C2 ⁱⁱⁱ —Hf1—C1	130.0 (2)
C2 ⁱ —Hf1—C2	126.86 (8)	C2 ^{iv} —Hf1—C1	94.8 (2)
C2 ⁱⁱ —Hf1—C2	53.1 (3)	C2—Hf1—C1	32.0 (2)
C2 ⁱⁱⁱ —Hf1—C2	101.55 (19)	C2 ^v —Hf1—C1	81.0 (2)
C2 ^{iv} —Hf1—C2	126.86 (8)	C1 ⁱ —Hf1—C1	122.45 (4)
C2 ⁱ —Hf1—C2 ^v	126.86 (8)	C1 ⁱⁱⁱ —Hf1—C1	112.98 (12)
C2 ⁱⁱ —Hf1—C2 ^v	126.86 (8)	C1 ^{iv} —Hf1—C1	122.45 (4)
C2 ⁱⁱⁱ —Hf1—C2 ^v	101.55 (19)	C1 ^v —Hf1—C1	112.98 (12)
C2 ^{iv} —Hf1—C2 ^v	53.1 (3)	C2 ⁱ —Hf1—C1 ⁱⁱ	130.0 (2)
C2—Hf1—C2 ^v	101.55 (19)	C2 ⁱⁱ —Hf1—C1 ⁱⁱ	32.0 (2)
C2 ⁱ —Hf1—C1 ⁱ	32.0 (2)	C2 ⁱⁱⁱ —Hf1—C1 ⁱⁱ	152.1 (2)
C2 ⁱⁱ —Hf1—C1 ⁱ	81.0 (2)	C2 ^{iv} —Hf1—C1 ⁱⁱ	81.0 (2)
C2 ⁱⁱⁱ —Hf1—C1 ⁱ	52.7 (2)	C2—Hf1—C1 ⁱⁱ	52.7 (2)
C2 ^{iv} —Hf1—C1 ⁱ	130.0 (2)	C2 ^v —Hf1—C1 ⁱⁱ	94.8 (2)
C2—Hf1—C1 ⁱ	94.8 (2)	C1 ⁱ —Hf1—C1 ⁱⁱ	112.98 (12)
C2 ^v —Hf1—C1 ⁱ	152.2 (2)	C1 ⁱⁱⁱ —Hf1—C1 ⁱⁱ	122.45 (4)
C2 ⁱ —Hf1—C1 ⁱⁱⁱ	52.7 (2)	C1 ^{iv} —Hf1—C1 ⁱⁱ	112.98 (12)
C2 ⁱⁱ —Hf1—C1 ⁱⁱⁱ	94.8 (2)	C1 ^v —Hf1—C1 ⁱⁱ	122.45 (4)
C2 ⁱⁱⁱ —Hf1—C1 ⁱⁱⁱ	32.0 (2)	C1—Hf1—C1 ⁱⁱ	31.4 (3)
C2 ^{iv} —Hf1—C1 ⁱⁱⁱ	152.2 (2)	C1 ⁱⁱ —C1—C2	108.3 (4)
C2—Hf1—C1 ⁱⁱⁱ	81.0 (2)	C1 ⁱⁱ —C1—Hf1	74.32 (14)
C2 ^v —Hf1—C1 ⁱⁱⁱ	130.0 (2)	C2—C1—Hf1	72.9 (4)
C1 ⁱ —Hf1—C1 ⁱⁱⁱ	31.4 (3)	C1 ⁱⁱ —C1—H1	125.9
C2 ⁱ —Hf1—C1 ^{iv}	81.0 (2)	C2—C1—H1	125.9
C2 ⁱⁱ —Hf1—C1 ^{iv}	130.0 (2)	Hf1—C1—H1	118.7
C2 ⁱⁱⁱ —Hf1—C1 ^{iv}	94.8 (2)	C3—C2—C1	107.3 (6)
C2 ^{iv} —Hf1—C1 ^{iv}	32.0 (2)	C3—C2—Hf1	75.3 (5)
C2—Hf1—C1 ^{iv}	152.2 (2)	C1—C2—Hf1	75.0 (4)
C2 ^v —Hf1—C1 ^{iv}	52.7 (2)	C3—C2—H2	126.4
C1 ⁱ —Hf1—C1 ^{iv}	112.98 (12)	C1—C2—H2	126.4
C1 ⁱⁱⁱ —Hf1—C1 ^{iv}	122.45 (4)	Hf1—C2—H2	115.6
C2 ⁱ —Hf1—C1 ^v	94.8 (2)	C2—C3—C2 ⁱⁱ	108.7 (8)
C2 ⁱⁱ —Hf1—C1 ^v	152.2 (2)	C2—C3—Hf1	73.0 (5)
C2 ⁱⁱⁱ —Hf1—C1 ^v	81.0 (2)	C2 ⁱⁱ —C3—Hf1	73.0 (5)
C2 ^{iv} —Hf1—C1 ^v	52.7 (2)	C2—C3—H3	125.6

C2—Hf1—C1 ^v	130.0 (2)	C2 ⁱⁱ —C3—H3	125.6
C2 ^v —Hf1—C1 ^v	32.0 (2)	Hf1—C3—H3	120.2

Symmetry codes: (i) $-x+y, -x+1, -z+1/2$; (ii) $x, y, -z+1/2$; (iii) $-x+y, -x+1, z$; (iv) $-y+1, x-y+1, -z+1/2$; (v) $-y+1, x-y+1, z$.