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

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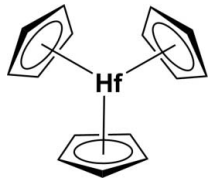
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.010 Å; R factor = 0.034; wR factor = 0.076; data-to-parameter ratio = 13.4.

In the crystal structure of the title compound, $[Hf(C_5H_5)_3]$, three cyclopentadienyl ligands surround the Hf^{III} atom in a trigonal–planar geometry. The molecule lies on a sixfold inversion axis.

Related literature

Isotypic $(\eta^5\text{-}C_5H_5)_3Zr$ was described by Lukens & Andersen (1995). For $(\eta^5\text{-}C_5H_5)_3M$, M = Y: see Adam *et al.* (1991); M = Nd: see Eggers *et al.* (1992*a*); M = Sm: see Wong *et al.* (1969), Bel'skii *et al.* (1991), Eggers *et al.* (1992*b*); M = Er, Tm: see Eggers *et al.* (1986); M = Yb: see Eggers *et al.* (1987); M = Ce, Dy, Ho: see Baisch *et al.* (2006). Unit-cell dimensions of $(\eta^5\text{-}C_5H_5)_3M$ (M = Pr, Pm, Sm, Gd, Tb, Tm, Cm, Bk, Cf) were determined by Laubereau & Burns (1970*a*,*b*).



Experimental

Crystal data

$[Hf(C_5H_5)_3]$
M_r = 373.76
Hexagonal, $P6_3/m$
a = 7.9772 (4) Å
c = 10.2975 (6) Å
V = 567.50 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 9.16 mm^{-1}
T = 150 K
0.30 × 0.20 × 0.15 mm

Data collection

Stoe IPDS II diffractometer
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_{int} = 0.097

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.076
S = 1.22
362 reflections
27 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −3.40 e Å^{-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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Tris(η^5-cyclopentadienyl)hafnium(III)

Vladimir V. Burlakov, Perdita Arndt, Anke Spannenberg and Uwe Rosenthal

S1. Comment

In the reaction of $(\eta^5\text{-}C_5H_5)_2Hf[—C(SiMe_3)═C(C≡CSiMe_3)— C(SiMe_3)═C(C≡CSiMe_3)—]$ with $(i\text{-}Bu)_2AlH$ 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). $(\eta^5\text{-}C_5H_5)_3Hf$ crystallizes in the hexagonal space group $P6_3/m$ 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 $(\eta^5\text{-}C_5H_5)_2Hf[—C(SiMe_3)═C(C≡CSiMe_3)—C(SiMe_3)═C(C≡CSiMe_3)—]$ was dissolved in 20 ml of *n*-hexane under Ar, and 2.6 ml (2.6 mmol) of a 1.0 *M* solution of $(i\text{-}Bu)_2AlH$ 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 $(\eta^5\text{-}C_5H_5)_3Hf$. Yield 9.3% (23 mg). *M*.p. 261–263 °C (dec. under Ar). MS (70 eV, m/*z*): 375 (M^+), 310 (M^+-C_5H_5).

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.

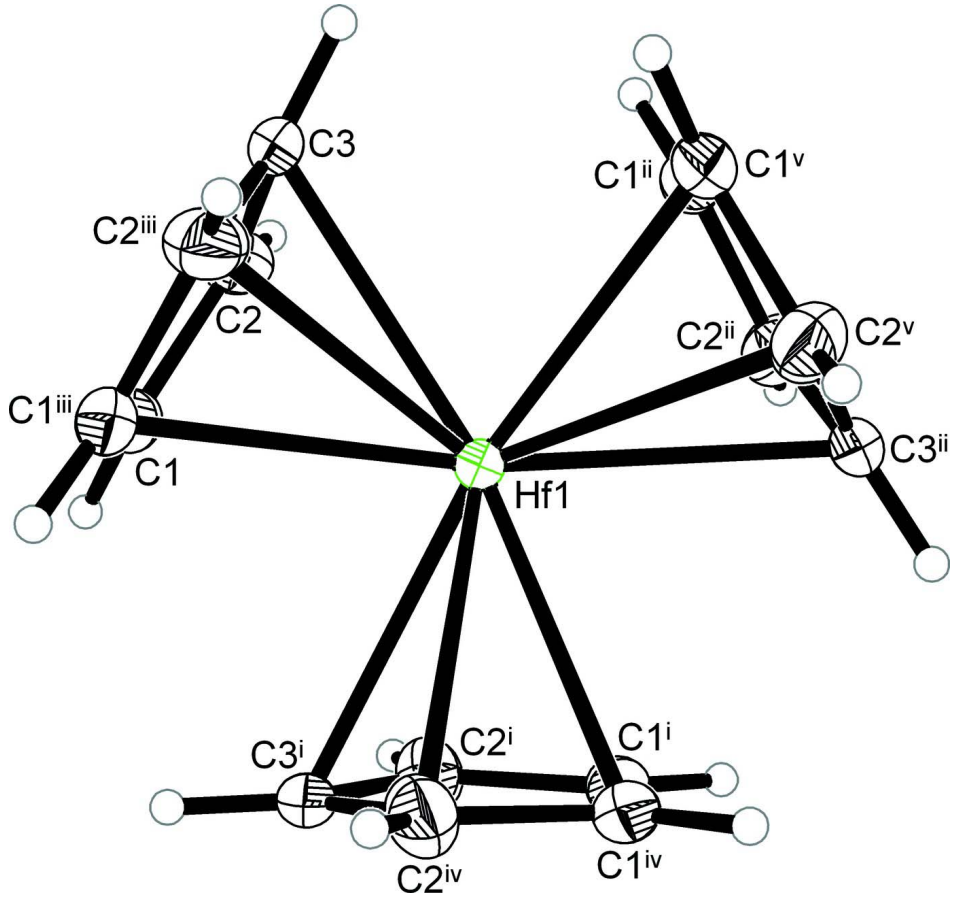

Figure 1

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

$[Hf(C_5H_5)_3]$
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) Å^3
Z = 2
F(000) = 354
D_x = 2.187 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4609 reflections
θ = 1.9–28.4°
μ = 9.16 mm^{-1}
T = 150 K
Prism, yellow
0.30 × 0.20 × 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_{int} = 0.097
θ_{max} = 25.0°, θ_{min} = 3.0°
h = −9→9
k = −9→9
l = −12→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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −3.40 e Å^{-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 (Å²)

	x	y	z	U_{iso}*/U_{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 (Å²)

	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 (Å, º)

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*.