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Tribenzyl(η^5-pentamethylcyclopentadienyl)hafnium(IV)

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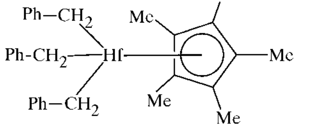
The title compound, [Hf(C_7H_7)$_3$($C_{10}H_{15}$)], adopts a monomeric three-legged piano-stool structure. One benzyl ligand is disordered between two sites (44:56%) related by a ~30° rotation about an axis defined by the Hf atom and the *ipso*-C atom of the benzyl ligand.

Comment

The structures of electronically unsaturated early transition metal benzyl complexes are often distorted by weak $M\cdots$Ph interactions which lead to reduced M—CH$_2$—Ph angles and short $M\cdots C_{ipso}$ contacts. Such η^2- or η^n-benzyl structures were first observed for M(CH$_2$Ph)$_4$ (M = Ti, Zr, Hf) complexes (Davies *et al.*, 1971; Bassi *et al.*, 1971) and have since been observed in a variety of systems, including cationic group 4 metal benzyl compounds (Jordan *et al.*, 1987, 1990; Crowther *et al.*, 1993; Bei *et al.*, 1997).

The title compound, (I), adopts a monomeric three-legged piano-stool structure. The plane formed by the three methylene C atoms (C11, C21*A* and C21*B* average, and C31) is parallel to the pentamethylcyclopentadienyl (Cp*) plane (dihedral angle = 0.5°). The Cp* methyl groups are bent slightly away from the Hf atom, with the largest deviation [0.166 (10) Å from the C1–C5 plane] occurring with the C10-methyl group that is eclipsed with the disordered benzyl ligand [C21*A*—C27*A*, occupancy = 0.44 (3); C21*B*—C27*B*, occupancy = 0.56 (3)]. There are no short Hf$\cdots C_{ipso}$ contacts (no distances less than 3.1 Å), indicating no significant Hf–Ph interactions.



(I)

Experimental

A solution of PhCH$_2$MgCl (10.2 ml, 2.0 *M* in tetrahydrofuran, 20.4 mmol) was added to a slurry of Cp*HfCl$_3$ (2.60 g, 6.19 mmol) in Et$_2$O (30 ml) at 195 K under nitrogen. The reaction mixture was warmed to room temperature and stirred for 1 h, resulting in a pale-yellow slurry. The solvent was removed under vacuum and the resultant solid was extracted with hexane (3 × 40 ml), giving a yellow filtrate. The filtrate was evaporated under vacuum to give a yellow solid which was further purified by recrystallization from toluene/hexane (1.34 g, 36.3%). Crystals suitable for X-ray diffraction were grown from a saturated toluene/hexane solution cooled to 238 K. Analysis calculated for $C_{31}H_{36}$Hf: C 64.42, H 6.18; found: C 64.50, H 5.99%. ^{1}H NMR (C$_6$D$_6$, 298 K) δ 7.14 (*t*, J = 7.6 Hz, 6H, *meta*), 6.91 (*t*, J = 7.6 Hz, 3H, *para*), 6.66 (*d*, J = 7.2 Hz, 6H, *ortho*), 1.7 (*s*, 15H, Cp*), 1.68 (*s*, 6H, CH$_2$). The low-temperature ^{1}H NMR spectrum (toluene-d_8, 203 K) is essentially unchanged from that at ambient temperature. ^{13}C{H} NMR (C$_6$D$_6$, 298 K): δ 145.9 (*ipso*-Ph), 128.8, 128.3, 122.9, 119.3 (C$_5$Me$_5$), 83.8 (*t*, J_{CH} = 121.4 Hz, from gated-{^{1}H} spectrum, HfCH$_2$), 11.7 (C$_5$Me$_5$).

Crystal data

[Hf(C_7H_7)$_3$($C_{10}H_{15}$)]
M_r = 587.09
Triclinic, $P\overline{1}$
a = 10.359 (1) Å
b = 12.693 (2) Å
c = 10.102 (7) Å
α = 97.49 (3)°
β = 91.42 (2)°
γ = 94.96 (1)°
V = 1311.1 (9) Å^3

Z = 2
D_x = 1.487 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40 reflections
θ = 6.5–10.2°
μ = 3.993 mm^{-1}
T = 293 (2) K
Prism, yellow
0.56 × 0.42 × 0.40 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
T_{min} = 0.154, T_{max} = 0.202
8828 measured reflections
4414 independent reflections
3907 reflections with $I > 2\sigma(I)$

R_{int} = 0.017
θ_{max} = 25°
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -11 \rightarrow 11$
4 standard reflections
frequency: 60 min
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.079$
S = 1.068
4414 reflections
353 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 1.4361P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.031$
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −1.01 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0117 (11)

Table 1
Selected geometric parameters (Å, °).

Hf1—C11	2.240 (5)	Hf1—C5	2.499 (5)
Hf1—C21*A*	2.23 (3)	Hf1—C3	2.499 (5)
Hf1—C21*B*	2.29 (2)	Hf1—C1	2.500 (5)
Hf1—C31	2.282 (6)	Hf1—C2	2.508 (5)
Hf1—C4	2.486 (5)		
C21*A*—Hf1—C11	97.3 (6)	C11—Hf1—C21*B*	106.8 (5)
C21*A*—Hf1—C31	117.2 (7)	C31—Hf1—C21*B*	103.4 (7)
C11—Hf1—C31	110.0 (2)		

Dale C. Swenson *et al.* • [Hf(C_7H_7)$_3$($C_{10}H_{15}$)] **e313**

One benzyl ligand (designated with C2** labels) was found to be disordered with two orientations; one is related to the other by a rotation of ~30° about an axis approximated by the Hf—(C22*A*/C22*B* average) direction. The occupancies refined to 0.44 (3) for the C2**A* site and 0.56 (3) for the C2**B* site. Each ligand was refined with individual anisotropic displacement parameters subject to the following restraints: (i) the ring C—C bonds were restrained to 1.39 (1) Å; (ii) the C22*A* and C22*B* atoms were assigned the same thermal displacement due to their close proximity (0.138 Å); (iii) each partial benzyl group was restrained to be flat (s.u. = 0.1); (iv) the rigid-bond restraint (s.u. = 0.005) was applied to the displacement parameters of each partially occupied benzyl group; (v) displacement parameters of atoms between the two sites were restrained to be similar if within 0.6 Å (s.u. = 0.05); (iv) the two sites were restrained to have the same conformation and bonds on opposite sides of the phenyl rings were restrained to be the same (default s.u.'s). H atoms were included with the riding model using program defaults.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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