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Di- μ -chloro-bis[chloro(η^5 -indenyl)methyl-hafnium(IV)]

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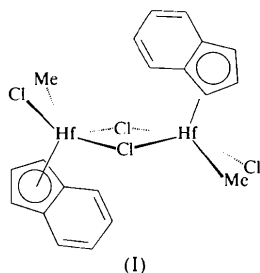
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Abstract

The molecular structure of the title complex, $[\text{HfCl}(\mu\text{-Cl})(\text{CH}_3)(\eta^5\text{-C}_9\text{H}_7)]_2$, which is a rare example of an indenylhafnium alkyl complex, is described. In this centrosymmetric structure, the geometry around each Hf atom is best described as a pseudo-square pyramid. There is a small amount of disorder between the methyl groups and the terminal chloride ligands.

Comment

The structural analysis of the title compound, (I), shows that it is composed of chloride-bridged dimers arranged in the $P2_1/n$ space group, and is structurally similar to $[\text{HfCl}_2(\mu\text{-Cl})(\eta^5\text{-C}_9\text{H}_7)]_2$ (Shaw & Morris, 1995). The dimer possesses a crystallographically imposed inversion center, and the molecule consists of two edge-sharing distorted square pyramids. As is the case in virtually every η^5 -indenyl



(Ind) structure, the two bridgehead C atoms of (I) form longer bonds with the Hf center [mean Hf—C_{bridgehead} distance = 2.519 (4) Å] than do the allyl-like C atoms [mean Hf—C_{allyl} distance = 2.454 (6) Å]. These Hf—C_{indenyl} distances in (I) are similar to the Hf—C distances in $[\text{HfCl}_2(\mu\text{-Cl})(\eta^5\text{-C}_9\text{H}_7)]_2$ [mean Hf—C_{bridgehead} distance = 2.526 (11) Å and mean Hf—C_{allyl} distance = 2.435 (11) Å], and show basically the same difference between Hf—C_{allyl} and Hf—C_{bridgehead} distances. The Hf—centroid distance in (I) of 2.164 Å is slightly longer than that in $[\text{HfCl}_2(\mu\text{-Cl})(\eta^5\text{-C}_9\text{H}_7)]_2$ of 2.154 Å. The terminal Hf—Cl distance of 2.398 (2) Å

is longer than the 2.337 (4)–2.354 (3) Å range reported for Hf—Cl distances in $[\text{Cp}^*\text{HfCl}_2\{\text{Si}(\text{SiMe}_3)_3\}]$ and $[\text{Cp}^*\text{HfCl}_2\{\text{Ge}(\text{SiMe}_3)_3\}]$ (Arnold *et al.*, 1988), but it is identical to the Hf—Cl distances of 2.391 (6) and 2.394 (6) Å in isopropyl(cyclopentadienyl-1-fluorenyl)-hafnium(IV) dichloride (Ewen *et al.*, 1988). The Hf—Cl_{terminal} distance of 2.398 (2) Å is also slightly longer than that of the average of 2.382 (4) Å for $[\text{HfCl}_2(\mu\text{-Cl})(\eta^5\text{-C}_9\text{H}_7)]_2$, as are the Hf—Cl_{bridging} distances {mean Hf—Cl_{bridging} distance = 2.566 (2) Å in (I) versus 2.526 (11) Å in $[\text{HfCl}_2(\mu\text{-Cl})(\eta^5\text{-C}_9\text{H}_7)]_2$ }. The bridging Hf—Cl distances in (I) of 2.565 (2) and 2.567 (2) Å represent symmetrical chloride bridges but, as expected, are longer than the terminal chloride distances. The Hf—C_{methyl} distance of 2.358 (3) Å is similar to the Hf—C_{methyl} distance in $\text{Ind}_2\text{Hf}(\text{CH}_3)_2$ [Hf—C_{methyl} = 2.332 (12) Å; Atwood *et al.*, 1975]. This increase is most likely a result of some disorder between the terminal Cl and the methyl C. The final occupancies are Cl3: 15.0(11)%C and 85.0(11)%Cl, and C4: 60.2(16)%C and 39.8(16)%Cl. Bond angles are as follows: Cl_{terminal}—Hf—C_{methyl} = 88.88 (9), Cl_{terminal}—Hf—Cl_{bridging} = 83.33 (6), *cis*-Cl_{bridging}—Hf—C_{methyl} = 82.64 (9), *trans*-Cl_{bridging}—Hf—C_{methyl} = 135.90 (9) and Cl_{bridging}—Hf—Cl_{bridging} = 75.54 (5)°. The indenyl plane [planar to within 0.046 (11) Å] is canted, so that the allyl-like C atoms are closest to the plane defined by the bridging Cl and Hf atoms. However, the indenyl ring is nearly parallel to the plane defined by an Hf atom, a terminal Cl and a methyl C atom. There is an angle of 57.16 (9)° between the plane of the bridging Cl atoms and the plane of the terminal Cl and methyl C atoms.

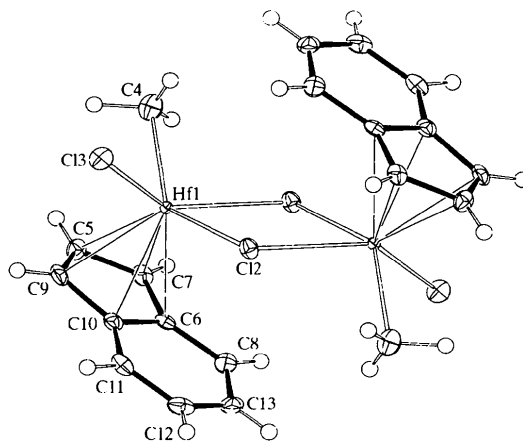


Fig. 1. Molecular structure diagram of (I) showing 35% probability displacement ellipsoids.

Experimental

The synthesis of (I) was carried out by the interaction of $[\text{HfCl}_2(\mu\text{-Cl})(\eta^5\text{-C}_9\text{H}_7)]_2$ with trimethylaluminium–toluene for 24 h. Recrystallization was from toluene.

Crystal data

[Hf ₂ Cl ₄ (CH ₃) ₂ (C ₉ H ₇) ₂]	Mo K α radiation
$M_r = 759.17$	$\lambda = 0.71069 \text{ \AA}$
Monoclinic	Cell parameters from 56 reflections
$P2_1/n$	$\theta = 9.59\text{--}10.30^\circ$
$a = 7.7771 (12) \text{ \AA}$	$\mu = 10.55 \text{ mm}^{-1}$
$b = 13.148 (2) \text{ \AA}$	$T = 100 \text{ K}$
$c = 10.0967 (15) \text{ \AA}$	Needle
$\beta = 90.944 (9)^\circ$	$0.13 \times 0.13 \times 0.11 \text{ mm}$
$V = 1032.3 (3) \text{ \AA}^3$	Orange
$Z = 2$	
$D_x = 2.442 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Refurbished Picker diffractometer	2015 reflections with $F^2 > 2.33\sigma(F^2)$
$\theta/2\theta$ scans	$R_{\text{int}} = 0.025$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.567, T_{\text{max}} = 0.743$	$h = -10 \rightarrow 3$
3330 measured reflections	$k = 0 \rightarrow 17$
2366 independent reflections	$l = -13 \rightarrow 13$
	4 standard reflections every 400 reflections
	intensity decay: -1.3%

Refinement

Refinement on F	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
$R = 0.028$	$\Delta\rho_{\text{min}} = 0.20 \text{ e \AA}^{-3}$
$wR = 0.028$	Extinction correction: Larson (1967)
$S = 1.259$	Extinction coefficient: $0.5 (3) \times 10^{-7}$
2015 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
161 parameters	
All H atoms refined	
$w = 1/[\sigma^2(F) + (0.04F)^2]$	
$(\Delta/\sigma)_{\text{max}} = 0.05$	

Table 1. Selected geometric parameters ($\text{\AA}, ^\circ$)

Hf1—Cl2	2.5649 (16)	Hf1—C6	2.519 (6)
Hf1—Cl2 ¹	2.5668 (15)	Hf1—C7	2.453 (6)
Hf1—Cl3	2.3977 (18)	Hf1—C9	2.450 (6)
Hf1—C4	2.358 (3)	Hf1—C10	2.519 (6)
Hf1—C5	2.459 (6)		
Cl2—Hf1—Cl2 ¹	75.54 (5)	Cl2 ¹ —Hf1—C4	135.90 (9)
Cl2—Hf1—Cl3	138.76 (6)	Cl3—Hf1—C4	88.88 (9)
Cl2 ¹ —Hf1—Cl3	83.33 (6)	Hf1 ¹ —Cl2—Hf1	104.46 (5)
Cl2—Hf1—C4	82.64 (9)		

Symmetry code: (i) $1 - x, -y, 2 - z$.

The structure was readily solved by direct methods (*MULTAN78*; Main *et al.*, 1978) and standard Fourier techniques. During refinement it was observed that some disorder is present between the terminal methyl and terminal chloride groups. The refinement results are: Cl3 = 15.0(11)%C and 85.0(11)%Cl, while C4 = 60.2(16)%C and 39.8(16)%Cl. Given that occupancy refinement is highly correlated with displacement parameters, the above may or may not indicate the presence of a small amount of [HfCl₂(μ -Cl)(η^5 -C₉H₇)₂], in spite of the reported s.u.'s. H atoms were refined [$U_{\text{iso}} = 0.01 (2)\text{--}0.06 (2) \text{ \AA}^2$] to yield C—H bond distances in the range 0.82 (15)–1.07 (12) \AA .

Data collection: *PCPS* (local software). Cell refinement: *XTEL* (local software). Data reduction: *XTEL*. Program(s) used

to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *XTEL*. Molecular graphics: *XTEL*. Software used to prepare material for publication: *XTEL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1091). Services for accessing these data are described at the back of the journal.

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2:1 Adducts of Halotris(*p*-tolyl)tin(IV) with 1,9-Bis(4-oxopent-2-en-2-ylamino)-3,7-dithianonane

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Abstract

The structures of (μ -5,15-diaza-8,12-dithianadeca-3,16-diene-2,18-dione-*O,O'*bis[halotris(*p*-tolyl)tin] {halo is bromo, [Sn₂Br₂(C₇H₇)₆(C₁₇H₃₀N₂O₂S₂)], iodo, [Sn₂-