

Group 4 Metal Polyhydrides: Synthesis, Structure, and Reactivity of Tetrakis[(pentamethylcyclopentadienyl)hafnium dihydride chloride]

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The polyhydride $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$ ² was prepared by high-pressure hydrogenation of $\text{Cp}^*\text{Hf}(\text{C}_6\text{H}_{10})\text{Cl}$ (C_6H_{10} = 2,3-dimethyl-1,3-butadiene) or $\text{Cp}^*\text{Hf}(\text{COT})\text{Cl}$ (COT = cyclooctatetraene). The structure of $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$ was determined by X-ray diffraction. The compound crystallizes in the tetragonal space group $P4_2/m$ with $a = 21.454$ (3) Å, $c = 10.525$ (3) Å, and $Z = 4$. The structure was refined to $R = 0.030$ and $R_w = 0.039$ for 303 parameters and 2839 reflections with $I > 2.5\sigma(I)$. The molecule has four Hf atoms in a butterfly arrangement with alternating Cp^* and Cl ligands (Hf-Ct = 2.15, 2.23, and 2.27 Å; Hf-Cl = 2.397 (3), 2.438 (3), and 2.432 (3) Å). Hydride positions could not be found due to disorder in one of the Cp^* ligands probably caused by the presence of a benzene solvate molecule. IR and NMR studies indicate the presence of two sets of four equivalent hydrides bridging the edges of a Hf_4 butterfly arrangement. Bridging hydride ligands account for the low reactivity of the complex.

Introduction

Most of the known early-transition-metal hydrides contain the Cp_2M moiety,^{3a,4a,b,5} and only few reports have been made on monocyclopentadienyl group 4 metal hydrides.⁶ The often successful method of hydrogenolysis of metal-carbon σ -bonds⁷ leads to polymeric products in the case of Cp^*ZrR_3 ^{6a} ($\text{R} = \text{Me}, \text{Ph}, \text{CH}_2\text{Ph}$), but use of bulky phosphide ligands allowed isolation of well-defined metal hydrides.^{6b} We tried to synthesize group 4 metal hydrides by the hydrogenolysis of well-defined metal hydrocarbyls Cp^*MMe_3 and $\text{Cp}^*\text{M}(\text{diene})\text{Cl}$ for $\text{M} = \text{Ti}, \text{Zr}$, or Hf.

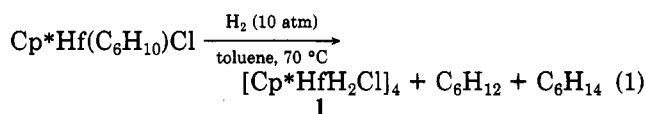
For $\text{M} = \text{Ti}$ hydrogenolysis resulted in partial reduction of the metal and formation of complicated mixtures in which titanium hydrides were present but could not be separated and identified in a pure state. For $\text{M} = \text{Zr}$ exploratory studies with the diene complexes were discouraging and not further investigated because of difficulties in obtaining the starting diene complexes.⁸ For $\text{M} = \text{Hf}$ the diene complexes proved to be convenient precursors for a hydride tetramer, $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$, on which we will focus our attention in the following.

Results and Discussion

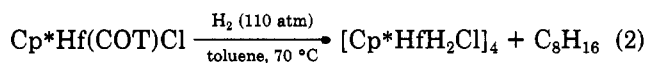
a. Synthesis. Our first strategy to obtain mono Cp^*Hf hydrides was based on the hydrogenolysis of Cp^*HfMe_3 .

This reaction under a variety of conditions⁹ led to the exclusive formation of methane in the gas phase (GC), but identification of the hafnium containing products was not possible. ¹H NMR showed complex mixtures with several resonances in the region characteristic for metal-bonded Cp^* ligands between 1.7 and 2.5 ppm. Hydrogenolysis of Cp^*HfMe_3 in the presence of Lewis bases such as THF and PMe_3 (stoichiometric amounts as well as excess) aimed at trapping intermediate hydride species did not lead to isolation of discrete Hf hydride species either. These observations are very similar to the hydrogenolyses of Cp^*ZrR_3 ($\text{R} = \text{alkyl}, \text{aryl}$) reported by Bercaw et al.^{6a}

We found that in contrast to Cp^*HfMe_3 , hydrogenolysis of the butadiene complex $\text{Cp}^*\text{Hf}(\text{C}_6\text{H}_{10})\text{Cl}$ (C_6H_{10} = 2,3-dimethyl-1,3-butadiene) proceeded in a straightforward way to give $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$ (1) in good yield (eq 1) (C_6H_{10} = 2,3-dimethyl-1,3-butadiene; C_6H_{12} = 2,3-dimethyl-2-butene; C_6H_{14} = 2,3-dimethylbutane). The deuteride analogue (1- d_5) was synthesized by using D_2 instead of H_2 . Under the reaction conditions applied the diene ligand was partially hydrogenated.



The fact that in cyclooctatetraene (COT) complexes this ligand is not always exactly η^8 -bonded^{6c,10} suggests that it may be regarded in $\text{Cp}^*\text{M}(\text{COT})\text{Cl}$ as a 1,4-disubstituted 1,3-diene in the series $\text{Cp}^*\text{M}(\text{diene})\text{Cl}$. A related reactivity was supposed, and indeed hydrogenolysis of $\text{Cp}^*\text{HfCOTCl}$ to $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$ took place, however, under conditions more drastic than necessary for the 1,4-unsubstituted system (eq 2) (C_8H_{16} = cyclooctane). The COT ligand was cleanly hydrogenated to cyclooctane (NMR).



b. Characterization. The ¹H NMR spectrum of 1 is very simple showing a singlet for the $\text{C}_5(\text{CH}_3)_5$ protons at

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(2) In this paper the following abbreviations are used: $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; Ct = ring centroid.

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(9) Reactions were carried out in toluene at pressures and temperatures ranging from 20 to 100 atm and 20 to 100 °C, respectively.

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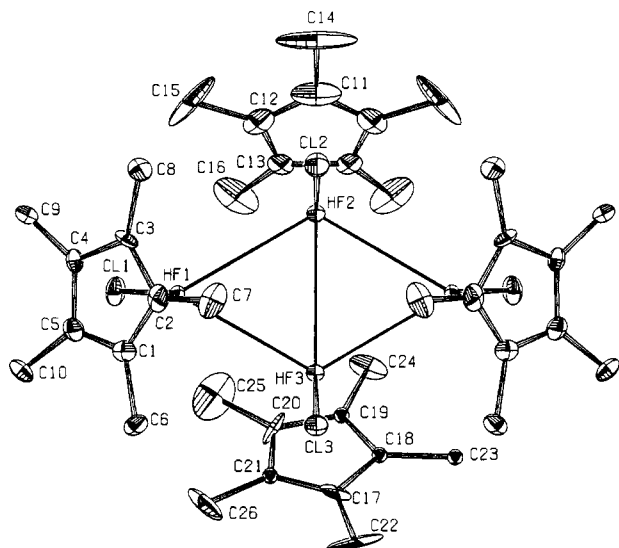


Figure 1. ORTEP drawing of $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$ (1). Only one position for the disordered Cp^* ligand attached to $\text{Hf}(3)$ is shown. Hydrogen atoms have been omitted for clarity. Symmetry-related atoms are noted in the text with the suffix B.

Table I. Selected Distances (Å) and Angles (deg) for $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$

a. Distances			
Hf(1)–Hf(2)	3.229 (1)	Hf(3)–Cl(3)	2.432 (3)
Hf(1)–Hf(3)	3.230 (1)	Hf(1)–Ct(1)	2.15
Hf(2)–Hf(3)	3.239 (1)	Hf(2)–Ct(2)	2.23
Hf(1)–Cl(1)	2.397 (3)	Hf(3)–Ct(3)	2.27
Hf(2)–Cl(2)	2.438 (3)		
b. Angles			
Hf(2)–Hf(1)–Hf(3)	60.20 (1)	Hf(1)–Hf(2)–Hf(1B)	117.88 (2)
Hf(1)–Hf(2)–Hf(3)	59.92 (1)	Ct(1)–Hf(1)–Cl(1)	110.0
Hf(1)–Hf(3)–Hf(2)	59.88 (1)	Ct(2)–Hf(2)–Cl(2)	108.1
Hf(1)–Hf(3)–Hf(1B)	117.81 (2)	Ct(3)–Hf(3)–Cl(3)	116.2

δ 2.30 and two broad resonances at δ 11.14 and 8.44 for the hydride ligands (ratio 1:1), which are absent in the ^1H NMR spectrum of the deuteride. A ^{13}C NMR spectrum could not be obtained due to the low solubility of the complex.

The IR spectrum of 1 shows, in addition to characteristic frequencies for the $\eta^5\text{-Cp}^*$ group, four broad absorptions due to Hf–H vibrations at 1575, 1320, 1130, and 890 cm^{-1} . These are shifted as expected in the deuteride to 1130, 940, 810, and 635 cm^{-1} , respectively. In general M–H vibrations above 1500 cm^{-1} are accepted as strong evidence for terminal M–H bonds,¹¹ but some bridging M–H bonds are known to have vibrational modes in this area as well^{5d,6b,12} and so IR is not sufficient to discriminate between bridging and terminal hydrides. An X-ray structure determination was undertaken in order to settle this problem.

c. Structure of $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$. The polyhydride $1 \cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$ was recrystallized from benzene. The crystals contained benzene in a ratio of one benzene per tetramer. The structure shown in Figure 1 shows that 1 is a tetramer of $\text{Cp}^*\text{HfH}_2\text{Cl}$ units with the four Hf atoms in a butterfly arrangement. A crystallographic mirror plane through Hf(2) and Hf(3) bisects the tetrameric unit. The short Hf–Hf distances (Table I) are 3.229 (1), 3.230 (1), and 3.239 (1) Å, which is about the sum of the atomic radii ($r_{\text{Hf}} =$

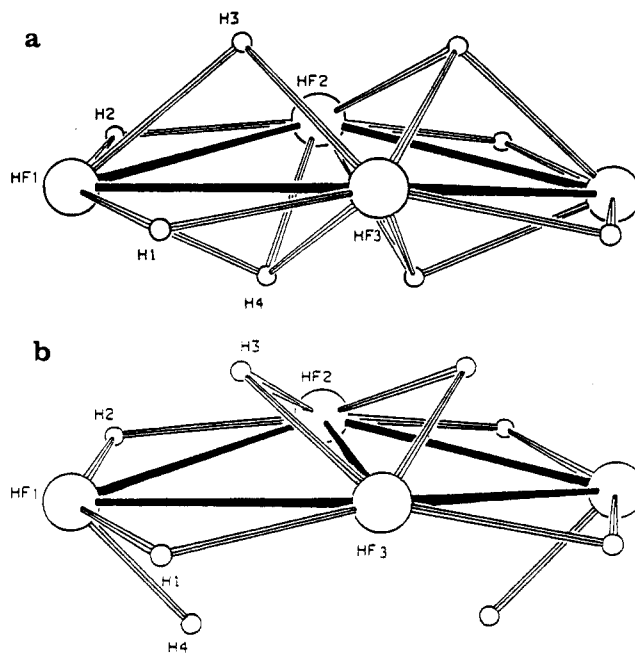


Figure 2. Hf_4 skeleton with two possible configurations, a and b, for the hydride ligands.

159 pm).¹³ Any direct Hf–Hf interaction can be excluded. The dihedral angle between the planes formed by the two equilateral triangles Hf(1)–Hf(2)–Hf(3) (A) and Hf(1B)–Hf(2)–Hf(3) (B) is 16.26 (3)°. The positions of the Cl and Cp^* ligands alternate with respect to the Hf_4 butterfly, thus providing an optimal shielding of the inner core of the molecule. Hf(2) and Hf(3) have a coordination sphere different from Hf(1) and Hf(1B) ($x_{\text{B}} = 0.5 - y$, $y_{\text{B}} = 0.5 - x$, $z = z_{\text{B}}$) as is reflected in the considerably longer Hf–Cl distances of 2.438 (3) and 2.432 (3) Å versus 2.397 (3) Å and Hf–Ct distances of 2.27 and 2.23 Å versus 2.15 Å. This suggests that the coordination number of Hf(2) and Hf(3) is higher than that of Hf(1) and Hf(1B).¹⁴ Both distances are comparable with those found in the complexes $(\text{CH}_2)_3(\text{C}_6\text{H}_4)_2\text{HfCl}_2$ (Hf–Ct = 2.17 and 2.18 Å, Hf–Cl = 2.423 (6) Å)¹⁵ and $\text{Cp}^*\text{Hf}(\text{C}_6\text{H}_{10})\text{Cl}$ (Hf–Ct = 2.216 Å, Hf–Cl = 2.393 (2) Å).⁸ The unit cell contains four benzene molecules on two crystallographically different positions. In one position the solvate molecule is sandwiched by the Cp^* rings of two tetramers, probably causing a disorder in the Cp^* ring attached to Hf(3).¹⁶ All Cp^* ligands are essentially η^5 -bonded with identical (C–C)_{ring} and C–CH₃ distances within error limits. The methyl groups bent away from the metal (average out of plane deviations of the methyl groups are 0.13 and 0.18 Å for rings attached to Hf(1) and Hf(2), respectively) which is common for early-transition-metal compounds.¹⁷

The hydride ligands could not be located despite several approaches to find them (see Experimental Section). The long Hf–Hf distances exclude metal–metal bonds and make it clear that hydride ligands hold the four Hf atoms together. ^1H NMR indicates that in solution the Cp^*

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ligands are equivalent on the NMR time scale and that the hydride ligands are grouped in two sets (ratio 1:1) of magnetically equivalent ligands. These hydrides are not interconverting in a slow dynamic process. Spin saturation transfer experiments did not show saturation transfer between the two hydride signals. Also raising the temperature does not lead to broadening of the signals, indicative for a high-temperature exchange process, so the conclusion seems justified that the two sets of hydride ligands are inequivalent in the tetramer over a broad temperature range.

An explanation for this observed inequivalence is that one set of four hydride ligands is bridging the exterior Hf–Hf edges of the butterfly and remains in that position as long as the tetramer exists. For the location of the other hydride ligands two possibilities are conceivable which are given in Figure 2. The option (Figure 2a) with μ_3 -hydrides capping the equilateral triangles A and B above and below the plane is not very likely. Although the equivalence of the hydrides could easily be realized by flapping the wings of the butterfly, the apparent equivalence of the Cp* ligands is hard to understand with this model. The other possibility (Figure 2b) has two μ_2 -bridging hydrides across the Hf(2)–Hf(3) vector and two terminal hydrides on Hf(1) and Hf(1B). Exchange of the bridging and terminal hydrides can be realized by a process in which the tips of the wings Hf(1) and Hf(1B) come closer and the two terminal hydrides form a μ_2 -bridge with concomitant loosening of the Hf(2)–Hf(3) double bridge while the bridging hydrides become terminal. In support of this latter structure is the IR spectrum where the hydride vibration at 1575 cm^{-1} can be assigned to the terminal hafnium–hydride vibration in Figure 2b. Attempts to check the possibility of Figure 2b with NMR at low temperature to freeze out the process failed due to the low solubility of 1.

d. Reactivity. Reactivity studies of 1 showed that it is chemically rather inert. It reacts slowly with H_2O under the formation of H_2 and Hf oxides. With HCl 1 reacts quantitatively to give Cp^*HfCl_3 and the expected amount of H_2 . Compound 1 reacts with CO (50 atm, 50 °C), but the reaction is complicated and attempts to identify the products were unsuccessful. The presence of oligomeric $[\text{Cp}^*\text{Hf}(\text{O})\text{Cl}]_n$ (IR, NMR)¹⁸ was established. With MeX (X = Cl, I) no reaction was observed at room temperature. With THF, PMe_3 , or pyridine no reaction was observed up to 80 °C, and above this temperature 1 starts to decompose giving complicated mixtures (^1H NMR). This inertness parallels the properties of other bridging hydrides of Hf.^{6b}

Experimental Section

General Considerations. All compounds are air-sensitive. Manipulations were performed under nitrogen by using standard Schlenk line, glovebox (Braun MB-200), and vacuum line techniques. IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer as Nujol mulls between KBr disks. NMR spectra were recorded on a Bruker WH-90-DS spectrophotometer. Elemental analyses were carried out at the Micro-Analytical Department of our laboratory under the supervision of Mr. A. F. Hamminga. Solvents were distilled from Na/K alloy and degassed prior to use. Pressure reactions were carried out in a 300-mL Parr bench-top pressure vessel (no. 4561). $\text{Cp}^*\text{Hf}(\text{C}_6\text{H}_{10})\text{Cl}^8$ was prepared according to published procedures. Cp^*HfMe_3 was prepared similar to $\text{Cp}^*\text{HfMeCl}_2$ and $\text{Cp}^*\text{HfMe}_2\text{Cl}$.^{5b} $\text{Cp}^*\text{Hf}(\text{COT})\text{Cl}$ was prepared similar to $\text{Cp}^*\text{ZrCOTCl}$.^{8c} Hydrogen (Hoek-Loos, technical purity, 99.9%) and deuterium (Matheson, CP) were used without further pu-

Table II. Selected Details on the Structure Determination of $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$

Crystal Data	
empirical formula	$\text{C}_{40}\text{H}_{68}\text{Cl}_4\text{Hf}_4$
mol wt	1404.754
cryst system	tetragonal
space group, no.	$P4_2/m, 113$
a, Å	21.454 (3)
c, Å	10.525 (3)
Z	4
D(calcd), g cm^{-3}	2.033
F(000), electrons	2824
μ (calcd), cm^{-1}	87.2
approx cryst size, mm	$0.26 \times 0.30 \times 0.40$
Data Collection	
radiatn, Å	Mo K α , 0.710 73 (graphite monochromated)
temp, K	130
θ range (min, max), deg	1.34, 27.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 1.10 + 0.35 \tan \theta$
no. of equiv reflns	2834
total data	5884
unique data	3037
obsd data ($I > 2.5$ $\sigma(I)$)	2839
Refinement	
no. of refined parameters	303
final $R_F = \sum(F_o - F_c)/\sum F_o $	0.030
final $wR = [\sum(w(F_o - F_c)^2)/\sum w F_o ^2]^{1/2}$	0.039
weighting scheme	$1/\sigma^2(F)$
residual electron density in final diff Fourier map, $\text{e}/\text{\AA}^3$	–1.01, 1.12

Table III. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms^a

atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
Hf(1)	–0.14615 (2)	–0.17153 (2)	0.76064 (4)	0.0117 (1)
Hf(2)	–0.26576 (2)	–0.23424 (2)	0.89600 (6)	0.0154 (1)
Hf(3)	–0.19036 (2)	–0.30964 (2)	0.67814 (5)	0.0135 (1)
Cl(1)	–0.0581 (1)	–0.1775 (1)	0.9003 (3)	0.0243 (6)
Cl(2)	–0.3410 (1)	–0.1590 (1)	0.8147 (4)	0.0247 (8)
Cl(3)	–0.2172 (1)	–0.2828 (1)	0.4604 (3)	0.0187 (8)
C(1)	–0.1274 (5)	–0.1194 (4)	0.558 (1)	0.020 (3)
C(2)	–0.1876 (5)	–0.1036 (5)	0.593 (1)	0.025 (3)
C(3)	–0.1827 (4)	–0.0660 (4)	0.707 (1)	0.018 (3)
C(4)	–0.1187 (4)	–0.0603 (4)	0.731 (1)	0.017 (3)
C(5)	–0.0846 (5)	–0.0941 (5)	0.641 (1)	0.023 (3)
C(6)	–0.1095 (6)	–0.1524 (5)	0.430 (1)	0.024 (3)
C(7)	–0.2469 (6)	–0.1159 (5)	0.520 (1)	0.034 (4)
C(8)	–0.2349 (5)	–0.0307 (4)	0.771 (1)	0.027 (3)
C(9)	–0.0916 (5)	–0.0236 (5)	0.842 (1)	0.025 (3)
C(10)	–0.0137 (5)	–0.0962 (5)	0.633 (1)	0.023 (3)
C(11)	–0.3075 (6)	–0.1925 (6)	1.104 (2)	0.050 (5)
C(12)	–0.2427 (7)	–0.1815 (5)	1.106 (1)	0.035 (4)
C(13)	–0.2149 (5)	–0.2394 (5)	1.1107 (9)	0.023 (3)
C(14)	–0.3579 (8)	–0.1421 (8)	1.109 (2)	0.11 (1)
C(15)	–0.213 (1)	–0.1220 (7)	1.119 (1)	0.10 (1)
C(16)	–0.1457 (6)	–0.2502 (8)	1.137 (1)	0.056 (5)
C(17)	–0.1317 (4)	–0.3962 (4)	0.559 (1)	0.030 (6)
C(18) ^c	–0.1600 (4)	–0.4270 (4)	0.664 (1)	0.027 (8)
C(19) ^c	–0.1327 (4)	–0.4038 (4)	0.777 (1)	0.030 (8)
C(20)	–0.0873 (4)	–0.3587 (4)	0.743 (1)	0.027 (8)
C(21) ^c	–0.0866 (4)	–0.3540 (4)	0.608 (1)	0.025 (5)
C(22)	–0.1467 (7)	–0.4068 (7)	0.419 (1)	0.07 (1)
C(23) ^c	–0.2113 (6)	–0.4766 (6)	0.655 (2)	0.06 (1)
C(24)	–0.1492 (7)	–0.4239 (7)	0.912 (1)	0.035 (8)
C(25)	–0.0463 (7)	–0.3216 (7)	0.834 (1)	0.07 (1)
C(26)	–0.0448 (7)	–0.3109 (7)	0.529 (1)	0.07 (1)
C(27)	0.0449 (7)	0.4551 (7)	0.155 (2)	0.055 (5)
C(28)	0.0633 (7)	0.5165 (7)	0.157 (1)	0.054 (5)
C(29)	0.522 (2)	–0.022 (2)	0.258 (3)	0.16 (2)
C(30)	0.5419 (8)	–0.0419 (8)	0.367 (4)	0.11 (1)
C(31)	0.522 (1)	–0.022 (1)	0.481 (3)	0.09 (1)

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^a Estimated standard deviations given in parentheses. ^b $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. ^c Nonpositive definite temperature factors.

rification.

[Cp*HfH₂Cl]₄·0.5C₆H₅CH₃. **a.** A pressure vessel was filled with a solution of 3.11 g (7.2 mmol) of Cp*Hf(C₆H₁₀)Cl in 40 mL of toluene and charged with 10 atm of H₂. The reaction mixture was stirred overnight at 70 °C, excess H₂ was released, and the hot solution was transferred into a Schlenk vessel. When the solution was cooled to room temperature, a bright yellow precipitate was formed. The solvent was decanted and the precipitate redissolved in hot toluene. Slow cooling to -30 °C gave 1.47 g of **1** (1.0 mmol, 56%, yellow needles). Anal. Found (Calcd for 1·0.5C₇H₈): C, 36.25 (36.01); H, 5.02 (5.00), Cl, 9.79 (9.77). ¹H NMR (90 MHz, toluene-*d*₈, 70 °C, TMS): δ 2.30 (s, 15 H), 8.44 (br, 1 H), 11.14 (br, 1 H).

b. A pressure vessel was filled with a solution of 0.50 g (1.1 mmol) of Cp*Hf(COT)Cl in 50 mL of toluene and charged with 95 atm of H₂. The reaction mixture was heated to 70 °C and stirred for 4 days. After workup similar to procedure **a** 0.14 g of **1** (0.1 mmol, 35%) was isolated. Compound **1** is light sensitive and turns brown on exposure to daylight.

Reaction of 1 with HCl. An excess of HCl (0.24 mmol) was allowed to react with a suspension of 51 mg (0.035 mmol) of **1** in 10 mL of benzene at room temperature. Immediately an exothermic reaction took place and the bright yellow suspension turned off-white. After 0.5 h the gases were collected and passed through a liquid-N₂-cooled trap. The amount of noncondensable gases determined by Toepler pump analysis was 0.265 mmol (1.90 mmol/mmol of Hf) and consisted exclusively of H₂ (GC, MS). After the volatiles were removed, the residue appeared to be Cp*HfCl₃ (IR).

Structure Determination. Suitable crystals for X-ray diffraction were obtained by cooling of a saturated hot benzene solution of **1**. A single crystal was glued on the top of a glass fiber and transferred into the nitrogen stream (130 K) of the low-temperature unit mounted on a Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Lattice parameters were derived from the angular settings of 24 reflections in the range 9.59° < θ < 20.16°. Selected data on the structure determination and atomic coordinates are given in Tables II and III, respectively.

The Hf and Cl atoms were found by using direct methods (MULTAN).¹⁹ Extension of the model was accomplished by using

standard Fourier techniques. It was obvious from the preliminary Fourier syntheses that the Cp* group [C(17)---C(26)] was disordered over a mirror plane.¹⁶ An idealized Cp* group was fit on the largest peaks and refined as a rigid group with *s*o_fs of 0.5. The method of Ibers and Cromer²⁰ to find hydrogen atoms was used, but the hydride and other hydrogens could not be located. Hydrogen atoms were introduced on calculated positions (*d*(C-H) = 1.0 Å) at C(6)–C(10), C(15), and C(16), included in the refinement as a rigid group with their carrier C atom, and subsequently refined satisfactorily. In the disordered Cp* group the atoms C(18), C(19), C(21), and C(23) converged to nonpositive definite thermal parameters when allowed to vary anisotropically. Refinement on *F* was carried out by block-diagonal least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms; hydrogen atoms were refined with one overall isotropic thermal parameter. A final difference Fourier was essentially featureless with the largest holes and peaks being 2.26 and 1.34 e/Å³ located near the Hf and Cl sites. Full details of the final refinements are included in the supplementary material.

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Supplementary Material Available: Full details on the structure determination and tables of all atomic coordinates, thermal parameters, bond distances, bond angles, torsion angles, and least-squares planes (25 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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