The Structures of Dimethylhafnocene and Its Hydrolysis Product, μ-Oxo-bis(methylhafnocene)

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Dimethylhafnocene, $(\eta^5$-$C_5H_5)_2Hf(CH_3)_2$, has been shown to undergo facile hydrolysis to form the oxygen-bridged product, μ-oxo-bis(methylhafnocene), $[(\eta^5$-$C_5H_5)_2HfCH_3]_2O$. The hydrolysis product has been characterized by infrared, proton NMR, and mass spectral techniques. The solid state structures of both these methylhafnium cyclopentadienyl complexes have been determined by single-crystal x-ray diffraction methods using counter data. Crystals of dimethylhafnocene are monoclinic, space group $P2_1/c$, and are isostructural with the analogous zirconium compound. Unit cell dimensions are a = 6.965 (2), b = 11.857 (4), c = 15.655 (6) Å, β = 118.38 (2)° with four molecules per unit cell. The oxo-bridged dimeric molecule crystallizes in the trigonal space group $P3_221$ with lattice constants a = 8.011 (2), c = 28.300 (8) Å, and three molecules per unit cell. In both compounds, the coordination geometry about hafnium is that of a distorted tetrahedron, and all cyclopentadienyl ligands are pentahapto bonded, having essentially equivalent Hf–C distances. Dimethylhafnocene has approximate C_{2v} molecular symmetry, with nonequivalent Hf–C(methyl) distances of 2.318 (8) and 2.382 (7) Å, and an average Hf–centroid distance of 2.210 Å. The Hf–C(methyl) distance appears to be very sensitive to intramolecular steric interactions. The dimeric complex has crystallographic C_2 symmetry and contains a nearly linear oxo bridge. The Hf–O–Hf angle is 173.9 (3)°, and the Hf–O distance is 1.941 (3) Å. The average Hf–centroid distance in this compound is 2.225 Å, and the Hf–C(methyl) distance is 2.295 (14) Å, substantially shorter than those in dimethylhafnocene. Full-matrix least-squares refinement using 3206 reflections led to weighted and unweighted R values of 0.045 and 0.036 for dimethylhafnocene and to corresponding values of 0.032 and 0.033 based on 1103 data for μ-oxo-bis(methylhafnocene).

Introduction

The widespread interest in organotitanium, and to a lesser extent organozirconium, chemistry during the past 20 years has been due in large measure to the activity of organometallic compounds of this type as catalysts in the polymerization of olefins and in the chemical fixation of nitrogen. In contrast, the organometallic chemistry of hafnium has only recently begun to emerge.[2] The first organometallic compound containing a carbon–hafnium σ bond was reported as recently as 1971,[3] and at the present time, only two x-ray structural studies dealing with σ-bonded organohafnium compounds have been described in the literature.[4,5] In order to obtain additional structural information on organohafnium compounds of this type, detailed single-crystal x-ray diffraction studies have been undertaken on dimethylhafnocene, $(\eta^5$-$C_5H_5)_2Hf(CH_3)_2$,[6] and its hydrolysis product, tetrakis(η^5-cyclopentadienyl)dimethyl-μ-oxo-dihafnium, $[(\eta^5$-$C_5H_5)_2HfCH_3]_2O$. These findings together with pertinent spectral results are presented in this paper.

Experimental Section

(A) Synthesis. A sample of $(\eta^5$-$C_5H_5)_2Hf(CH_3)_2$ was prepared as described previously.[6] To prepare the oxo-bridged material, dimethylhafnocene was dissolved in benzene and the solution exposed to air in the dark at room temperature for 45 h. The solution was centrifuged and the solvent was evaporated to yield $[(\eta^5$-$C_5H_5)_2HfCH_3]_2O$ as a white crystalline solid. NMR (C_6D_6) τ 9.85 (3 H), 4.22 (10 H); ir (KBr) 3100 (w), 2900 (m), 1430 (w), 1005 (s), 820 (sh), 760–790 (vs) cm⁻¹; mass spectrum, see Table VII.

(B) Crystallographic Characterizations and Data Collection. Crystals of dimethylhafnocene were grown by slow evaporation from dry pentane; crystals of μ-oxo-bis(methylhafnocene) and dimethylzirconocene were obtained by slow cooling of pentane solutions. Preliminary precession and Weissenberg photographs revealed that dimethylhafnocene and dimethylzirconocene have essentially identical monoclinic lattice dimensions and almost indistinguishable intensity distributions, demonstrating their isostructural nature. Systematic absences $h0l$ with l odd and $0k0$ with k odd uniquely determine the space group to be $P2_1/c$ (C_{2h}^5). The hafnium compound was chosen for three-dimensional structure elucidation. Precession photographs of the oxo-dimer crystals exhibited diffraction symmetry $\bar{3}m$ (D_{3d}) and systematic absences $00l$ with $l \neq 3n$, limiting space group possibilities to $P3_121$, or its enantiomorph $P3_221$.

Intensity data were collected by the θ–2θ scan technique using a Picker FACS-1 four-circle diffractometer at ambient temperature of 24 °C. The moisture- and air-sensitive crystals were mounted in

thin-walled glass capillaries under a dry nitrogen atmosphere. Lattice constants and orientation angles were determined from a least-squares refinement of setting angles for carefully centered high-angle reflections. Data were collected using graphite-monochromatized Mo Kα radiation at constant scanning rate with backgrounds counted for fixed intervals at each extreme of the scan, and scan widths were varied to accommodate α_1–α_2 dispersion. Copper foil attenuators were automatically inserted between the sample and the counter to prevent intensity losses due to excessive counting rates. In each case, three standard reflections were periodically remeasured as a check of instrument and crystal stability. Particular parameters used for the two experiments are tabulated in Table I, along with pertinent crystal data.

Decrease in intensities of standard reflections was used to correct measured intensities, and Lorentz and polarization corrections were applied. Observational variances were assigned from counting statistics with an additional term to account for nonstatistical fluctuations.[7] Absorption corrections were made by an analytical integration method,[8] after which equivalent reflections were averaged and placed upon an approximately absolute scale by the method of Wilson.[9]

Solution and Refinement of Structures. (A) Dimethylhafnocene. The position of the hafnium atom was easily determined from a Patterson synthesis, and phases based upon the heavy atom proved sufficient to locate all but three of the Cp carbon atoms, which were placed in calculated positions. Full-matrix least-squares refinement minimizing the function $\sum w(F_o^2 - F_c^2)^2$ where the weights are $w = 1/\sigma^2(F_o^2)$ converged rapidly. Atomic scattering factors for neutral hafnium and carbon were those tabulated by Cromer and Mann,[10] and those for hydrogen were as given by Stewart, Davidson, and Simpson for the bonded atom.[11] Correction for the effects of anomalous dispersion by the hafnium atom were made, including both the real and imaginary terms.[12] Near the end of anisotropic refinement, most of the cyclopentadienyl hydrogen atoms were located from difference maps; however, methyl hydrogen atom positions could not be discerned. Unclear Cp hydrogen atoms were placed in the plane of the ring with B = 5 Å². Hydrogen atom parameters were not refined. All measured reflections were used in the refinement, which was terminated when all shifts were less than 10% of the corresponding standard deviations. Final weighted and unweighted R factors[13] are 0.053 and 0.059, respectively, based upon the full set of 3206 reflections, and 0.045 and 0.036 based upon the 2408 reflections for which $F_o^2 > 3\sigma(F_o^2)$. The error in an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, is 1.52 for N_o = 3206 data and N_v = 118 variables. A difference synthesis calculated at the conclusion of the refinement exhibited features of density ±1.7 e Å⁻³ in the vicinity of the Hf atom and no other residuals of density greater than 0.8 e Å⁻³.

Positional and thermal parameters are tabulated in Table II, and

Table I. Crystal Data and Intensity Data Collection Summary

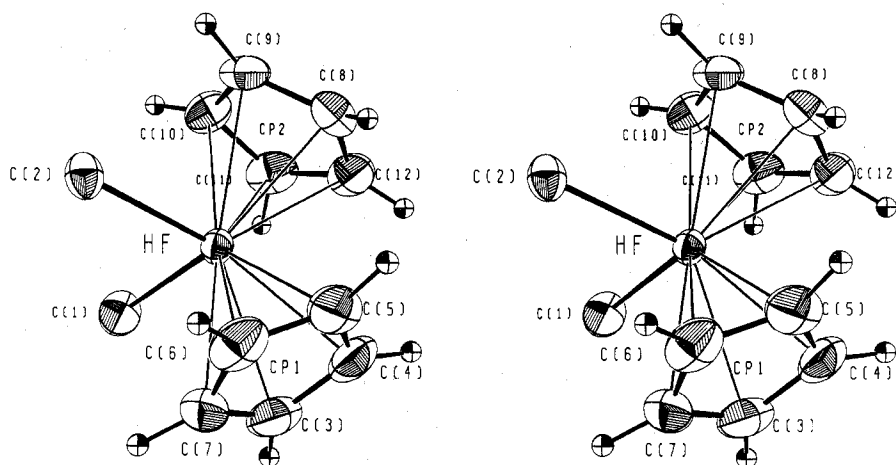|	$Hf(C_5H_5)_2(CH_3)_2$	$[Hf(C_5H_5)_2(CH_3)]_2O$
Mol formula	$Hf(C_5H_5)_2(CH_3)_2$	$[Hf(C_5H_5)_2(CH_3)]_2O$
Mol wt	338.64	663.43
Space group	$P2_1/c$, monoclinic	$P3_221$, trigonal
Formulas/cell	4	3
a, Å	6.965 (2)	8.011 (2)
b, Å	11.857 (4)	
c, Å	15.655 (6)	28.300 (8)
β, deg	118.38 (2)	
Cell vol, Å^3	1137	1573
Calcd density, g/cm^3	1.977	2.101
Linear absorption coeff, cm^{-1}	96.14	104.64
Absorption corr range	2.32–4.39	1.93–6.70
Crystal size	0.045 × 0.021 × 0.012 cm	0.028 × 0.022 × 0.006 cm
Data collected	$\pm h, k, \pm l$ to $2\theta = 30°$	$hkl, \bar{h}\bar{k}l,$ and $\bar{h}k\bar{l}$ to $2\theta = 40°$
	$\pm h, k, l$ to $2\theta = 60°$	$h\bar{k}l$ to $2\theta = 60°$
Scan rate	1°/min, $2\theta \leqslant 30°$	1°/min
	0.5°/min, $2\theta > 30°$	
Background time	20 s, $2\theta \leqslant 30°$	10 s
	40 s, $2\theta > 30°$	
Decline in standards	5% in F^2	10% in F^2
Scan width ($2\theta = 0$)	1.3° 2θ	1.5° 2θ
Radiation	Mo Kα_1, λ 0.709 261 Å	Mo Kα_1
Crystal mounted along	1° from a	18° from c^*
R	0.036	0.033
R_w	0.045	0.032

Figure 1. Stereoscopic drawing of the dimethylhafnocene molecule. Anisotropic thermal parameters are represented by 30% probability ellipsoids. Cyclopentadienyl hydrogen atoms are represented by spheres of arbitrary radius.

a table of calculated and observed structure factors is available.[14]

(B) μ-Oxo-bis(methylhafnocene). The presence of three molecules per unit cell in space group $P3_121$ (or its enantiomorph) necessitates that the molecule lie upon a twofold axis. A hafnium position in $P3_121$ which is consistent with the Patterson vectors led to location of the remainder of the molecule. Refinement was carried out in a manner similar to that described for dimethylhafnocene, based upon data for which $F_0^2 > 3\sigma(F_0^2)$ and minimizing the function $\sum w(|F_0| - |F_c|)^2$. Cyclopentadienyl hydrogen atoms were placed in calculated positions with $B = 8$ Å^2 and not refined. Refinement was terminated when all shifts were less than 0.1σ. The weighted R factor was 0.035, the unweighted R factor was 0.036, and the error in an observation of unit weight was 1.15 for 1103 observations and 114 refined parameters. At this point, refinement was attempted in $P3_221$, which was shown to be the correct enantiomorph. Weighted and unweighted R factors based upon this refinement are 0.032 and 0.033, and the error in an observation of unit weight is 1.06. This improvement is significant at better than the 99.5% probability level.[15] Of 32 reflections for which significant differences in F_c were observed between the two space groups, all but two fit the observed values better for $P3_221$. Positional and thermal parameters are tabulated in Table III, and a table of calculated and observed structure factors is available.[14]

Structure Descriptions and Discussion

The results of structure determinations of dimethylhafnocene and its dimeric μ-oxo derivative prove both to be typical "tilted π-sandwich" organometallic complexes. The coordination geometry about hafnium in both compounds is distorted
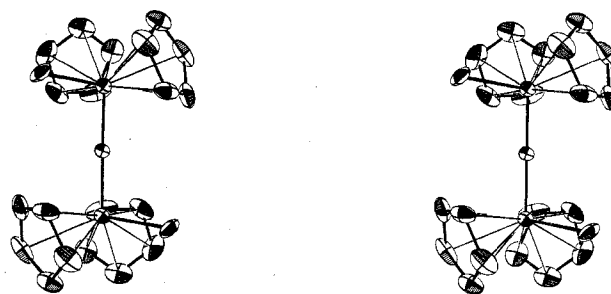

Figure 2. Stereoscopic drawing of μ-oxo-bis[methylhafnocene], viewed down the crystallographic twofold axis. Thermal ellipsoids are drawn at the 25% probability level, and hydrogen atoms are omitted for clarity.

tetrahedral, and the cyclopentadienyl rings are coordinated in the pentahapto mode, as illustrated in Figures 1 and 2. Dimethylhafnocene is crystallographically asymmetric, although deviations from ideal C_{2v} symmetry are small, and μ-oxo-bis(methylhafnocene) exhibits rigorous C_2 symmetry in the crystal. The (methylhafnocene) portion of the dimeric molecule is very similar in structure to the parent dimethyl complex.

Detailed comparisons of the molecular dimensions of these two metallocenes with those of similar compounds are difficult to draw, due to the scarcity of structural information for

Table II. Positional[a] and Thermal[b] Parameters (×10⁴) for Dimethylhafnocene

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hf	0.418 34 (4)	0.208 869 (20)	0.360 622 (17)	188.9 (7)	54.22 (19)	40.45 (14)	11.48 (14)	48.64 (23)	3.25 (12)
C(1)	0.149 6 (13)	0.344 2 (7)	0.2876 (6)	312 (23)	89 (7)	70 (5)	54 (10)	79 (9)	26 (4)
C(2)	0.229 4 (10)	0.106 7 (5)	0.4283 (5)	215 (16)	64 (5)	63 (4)	13 (7)	61 (7)	9 (3)
C(3)	0.343 5 (20)	0.177 1 (8)	0.1885 (6)	553 (42)	114 (8)	48 (4)	46 (15)	94 (11)	6 (4)
C(4)	0.557 6 (17)	0.150 7 (10)	0.2484 (7)	429 (11)	144 (11)	68 (5)	−51 (15)	122 (11)	−35 (6)
C(5)	0.559 7 (16)	0.053 7 (9)	0.2995 (6)	415 (30)	122 (9)	68 (5)	59 (14)	73 (10)	−19 (6)
C(6)	0.342 6 (18)	0.029 0 (8)	0.2671 (7)	572 (39)	87 (7)	89 (6)	−64 (14)	149 (14)	−36 (5)
C(7)	0.214 6 (13)	0.106 1 (8)	0.1995 (6)	278 (22)	119 (9)	62 (5)	3 (11)	52 (8)	−12 (5)
C(8)	0.796 9 (13)	0.212 5 (7)	0.4964 (6)	243 (19)	88 (6)	66 (5)	8 (9)	30 (8)	−8 (4)
C(9)	0.667 6 (16)	0.235 2 (7)	0.5396 (5)	370 (26)	94 (7)	41 (4)	−30 (11)	39 (8)	0 (4)
C(10)	0.564 6 (15)	0.337 5 (7)	0.5042 (6)	408 (29)	89 (6)	62 (5)	−5 (11)	91 (10)	−21 (4)
C(11)	0.638 7 (16)	0.381 7 (7)	0.4413 (6)	487 (32)	71 (6)	63 (5)	−52 (12)	81 (10)	−14 (4)
C(12)	0.787 4 (16)	0.302 7 (8)	0.4376 (6)	344 (27)	125 (9)	61 (5)	−92 (12)	75 (9)	−27 (5)
H(1)	0.295 1	0.242 1	0.1422						
H(2)	0.689 4	0.192 5	0.2539						
H(3)	0.693 9	−0.002 2	0.3466						
H(4)	0.287 6	−0.039 8	0.2902						
H(5)	0.051 8	0.109 3	0.1663						
H(6)	0.843 0	0.150 1	0.4885						
H(7)	0.626 4	0.157 0	0.5820						
H(8)	0.463 2	0.370 5	0.5140						
H(9)	0.563 9	0.449 0	0.3848						
H(10)	0.860 4	0.299 9	0.4022						

[a] Refined values have standard deviations of the least significant figure in parentheses. [b] The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Positional[a] and Thermal[b] Parameters (×10⁴) for $[(C_5H_5)_2HfCH_3]_2O$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hf	0.236 68 (6)	0.133 86 (5)	0.436 33 (1)	145.9 (9)	164.0 (10)	11.3 (1)	66.4 (9)	5.8 (2)	2.2 (2)
O	0.199 0 (10)	0.199 0 (10)	¹/₂	195 (15)	195 (15)	7 (1)	118 (16)	3 (2)	−3 (2)
C(Me)	−0.054 3 (14)	0.074 6 (17)	0.406 6 (3)	248 (26)	569 (44)	7 (1)	236 (28)	−16 (5)	−14 (6)
C(1,1)	0.251 2 (21)	−0.140 3 (14)	0.397 9 (4)	417 (42)	185 (26)	21 (2)	121 (29)	44 (9)	−1 (6)
C(1,2)	0.384 6 (17)	−0.079 4 (15)	0.433 8 (6)	283 (32)	199 (28)	34 (3)	154 (25)	14 (9)	−2 (8)
C(1,3)	0.274 9 (21)	−0.124 1 (16)	0.476 8 (4)	422 (41)	240 (30)	20 (2)	220 (32)	5 (9)	2 (7)
C(1,4)	0.089 9 (21)	−0.208 3 (13)	0.466 2 (5)	482 (47)	146 (23)	16 (2)	94 (29)	43 (9)	6 (5)
C(1,5)	0.062 0 (18)	−0.221 4 (13)	0.417 1 (5)	248 (32)	168 (24)	36 (3)	11 (24)	6 (10)	−34 (7)
C(2,1)	0.395 3 (30)	0.483 7 (18)	0.417 9 (8)	512 (62)	191 (31)	41 (5)	194 (41)	81 (15)	34 (9)
C(2,2)	0.330 3 (25)	0.398 8 (26)	0.376 0 (6)	620 (75)	414 (50)	15 (2)	240 (48)	19 (11)	54 (9)
C(2,3)	0.429 1 (26)	0.311 7 (19)	0.364 5 (5)	424 (52)	276 (36)	18 (2)	67 (36)	51 (9)	20 (7)
C(2,4)	0.558 9 (19)	0.336 9 (20)	0.396 8 (7)	215 (32)	372 (45)	27 (3)	47 (32)	40 (8)	40 (10)
C(2,5)	0.539 5 (25)	0.453 6 (26)	0.433 5 (4)	425 (49)	304 (40)	16 (2)	−293 (40)	38 (10)	−1 (10)
H(1,1)	0.279 7	−0.131 6	0.362 1						
H(1,2)	0.522 3	−0.021 4	0.429 9						
H(1,3)	0.331 0	−0.091 8	0.508 9						
H(1,4)	−0.015 6	−0.254 6	0.489 9						
H(1,5)	−0.060 5	−0.277 7	0.400 3						
H(2,1)	0.354 2	0.561 1	0.438 9						
H(2,2)	0.235 4	0.411 3	0.358 5						
H(2,3)	0.410 9	0.240 0	0.334 1						
H(2,4)	0.653 5	0.291 4	0.397 5						
H(2,5)	0.613 0	0.497 5	0.464 0						

[a] Refined values contain standard deviations of the least significant figure in parentheses; positions for hydrogen atoms are assigned. [b] The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

hafnium organometallics and to the non-innocent nature of such species as indenyl and 1,1′-trimethylenedicyclopentadienyl found in much of the recent work in the area. Structural differences might be anticipated between complexes of these ligands and those of the simple cyclopentadienyl anion, and indeed differences are noted.

Important distances and angles found in the dimethylhafnocene molecule are listed in Table IV, and those in the dimer are tabulated in Table V. The determination of the monomeric molecule is slightly more precise, having formal standard deviations in bond distances about 40% smaller than those of the dimer.

The pentahapto (η^5) coordination mode of the cyclopentadienyl rings in both compounds is apparent from examination of several structural parameters given in Tables IV and V. The Hf–C distances for the Cp rings of dimethylhafnocene fall in the fairly narrow range of 2.474 (9)–2.539

(9) Å, and average 2.505 (7) Å. The Hf–Cp (ring centroid) distances are essentially identical and average 2.210 Å. Corresponding values for the μ-oxo dimer are very similar, with Hf–C distances ranging from 2.487 (13) to 2.531 (13) Å and averaging 2.513 (5) Å. The average Hf–Cp distance of the dimeric molecule is 2.225 Å.

These values may be compared (with caution) with those found in the rather limited literature on structural hafnium organometallic chemistry. The only other structures which have been determined for hafnium compounds containing cyclopentadienide are those of HfCp₄[4] and Cp₂HfC₄-(C₆H₅)₄,[16] the former being of low precision. The mean Hf–C value reported for the pentahapto rings of HfCp₄ is 2.50 Å, and that reported for Cp₂HfC₄(C₆H₅)₄ is 2.49 Å, both in good agreement with our results. The precise determination of the structure of (CH₂)₃(C₅H₄)₄HfCl₂,[17] when compared to our results, demonstrates the close similarity in the bonding to
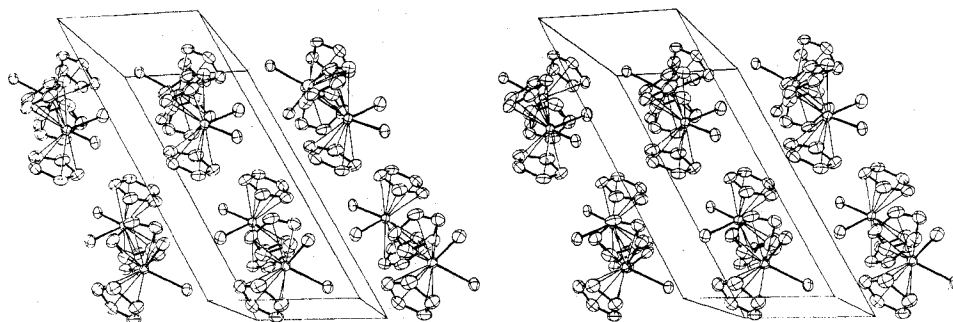
Figure 3. The crystal packing of dimethylhafnocene. The outlined area is one unit cell. The view direction is slightly oblique to b, with a horizontal.

Table IV. Important Distances and Angles of Dimethylhafnocene

Atoms	Distance, Å	Atoms	Distance, Å
	Methyl Groups		
Hf–C(1)	2.318 (8)	Hf–Cp1	2.214
Hf–C(2)	2.382 (7)	Hf–Cp2	2.207
	Cp1		
Hf–C(3)	2.523 (9)	C(3)–C(4)	1.370 (16)
Hf–C(4)	2.474 (9)	C(4)–C(5)	1.406 (16)
Hf–C(5)	2.475 (9)	C(5)–C(6)	1.373 (14)
Hf–C(6)	2.499 (8)	C(6)–C(7)	1.374 (14)
Hf–C(7)	2.539 (9)	C(7)–C(3)	1.303 (14)
	Cp2		
Hf–C(8)	2.479 (9)	C(8)–C(9)	1.387 (14)
Hf–C(9)	2.520 (8)	C(9)–C(10)	1.381 (14)
Hf–C(10)	2.500 (8)	C(10)–C(11)	1.409 (13)
Hf–C(11)	2.515 (8)	C(11)–C(12)	1.434 (15)
Hf–C(12)	2.528 (9)	C(12)–C(18)	1.396 (13)

Atoms	Angle, deg	Atoms	Angle, deg
C(1)–Hf–C(2)	94.8 (3)	C(1)–Hf–Cp2	105.9
Cp1–Hf–Cp2	132.1	C(2)–Hf–Cp1	106.0
C(1)–Hf–Cp1	106.0	C(2)–Hf–Cp2	105.9
C(3)–Hf–C(4)	31.8 (4)	C(8)–Hf–C(9)	32.2 (3)
C(4)–Hf–C(5)	33.0 (4)	C(9)–Hf–C(10)	31.9 (3)
C(5)–Hf–C(6)	32.0 (3)	C(10)–Hf–C(11)	32.6 (3)
C(6)–Hf–C(7)	31.6 (3)	C(11)–Hf–C(12)	33.0 (3)
C(7)–Hf–C(3)	29.8 (3)	C(12)–Hf–C(8)	32.4 (3)
C(3)–C(4)–C(5)	107.2 (10)	C(8)–C(9)–C(10)	108.6 (8)
C(4)–C(5)–C(6)	105.0 (9)	C(9)–C(10)–C(11)	108.1 (9)
C(5)–C(6)–C(7)	109.5 (9)	C(10)–C(11)–C(12)	107.6 (8)
C(6)–C(7)–C(3)	107.9 (9)	C(11)–C(12)–C(8)	106.1 (9)
C(7)–C(3)–C(4)	110.4 (9)	C(12)–C(8)–C(9)	109.5 (8)

Table V. Important Distances and Angles of
μ-Oxo-bis[methylhafnocene]

Atoms	Distance, Å	Atoms	Distance, Å
Hf–O	1.941 (3)	Hf–Cp1	2.222
Hf–C(Me)	2.295 (14)	Hf–Cp2	2.229
Hf–C(1,1)	2.503 (15)	Hf–C(2,1)	2.487 (13)
Hf–C(1,2)	2.518 (15)	Hf–C(2,2)	2.531 (13)
Hf–C(1,3)	2.505 (15)	Hf–C(2,3)	2.519 (15)
Hf–C(1,4)	2.527 (15)	Hf–C(2,4)	2.521 (15)
Hf–C(1.5)	2.523 (15)	Hf–C(2,5)	2.493 (15)
C(1,1)–C(1,2)	1.38 (2)	C(2,1)–C(2,2)	1.34 (2)
C(1,2)–C(1,3)	1.44 (2)	C(2,2)–C(2,3)	1.33 (2)
C(1,3)–C(1,4)	1.32 (2)	C(2,3)–C(2,4)	1.33 (2)
C(1,4)–C(1,5)	1.40 (2)	C(2,4)–C(2,5)	1.46 (2)
C(1,5)–C(1,1)	1.43 (2)	C(2,5)–C(2,1)	1.37 (2)

Atoms	Angle, deg	Atoms	Angle, deg
O–Hf–C(Me)	96.9 (5)	C(Me)–Hf–Cp1	104.0
O–Hf–Cp1	108.1	C(Me)–Hf–Cp2	103.7
O–Hf–Cp2	110.5	Cp1–Hf–Cp2	128.5
Hf–O–Hf	173.9 (3)		
C(1,1)–Hf–C(1,2)	31.9 (6)	C(2,1)–Hf–C(2,2)	31.0 (6)
C(1,2)–Hf–C(1,3)	33.4 (6)	C(2,2)–Hf–C(2,3)	30.6 (6)
C(1,3)–Hf–C(1,4)	30.3 (5)	C(2,3)–Hf–C(2,4)	30.5 (6)
C(1,4)–Hf–C(1,5)	32.2 (5)	C(2,4)–Hf–C(2,5)	33.7 (6)
C(1,5)–Hf–C(1,1)	33.0 (5)	C(2,5)–Hf–C(2,1)	31.8 (7)
C(1,1)–C(1,2)–C(1,3)	104.9 (15)	C(2,1)–C(2,2)–C(2,3)	107.4 (21)
C(1,2)–C(1,3)–C(1,4)	109.5 (17)	C(2,2)–C(2,3)–C(2,4)	112.3 (21)
C(1,3)–C(1,4)–C(1,5)	111.1 (17)	C(2,3)–C(2,4)–C(2,5)	105.1 (20)
C(1,4)–C(1,5)–C(1,1)	104.3 (16)	C(2,4)–C(2,5)–C(2,1)	105.0 (19)
C(1,5)–C(1,1)–C(1,2)	110.1 (15)	C(2,5)–C(2,1)–C(2,2)	110.1 (19)

hafnium(IV) of the innocent Cp ligand and the 1,1'-trimethylenedicyclopentadienyl group. The mean Hf–C distance in that structure is 2.482 (4) Å, only slightly smaller than those found here, and the range of distances is actually smaller than those in our structures. The structure of bis(indenyl)dimethylhafnium[5] has been determined, and shows a range of Hf–C distances for the five-membered ring of the indenyl groups which is about twice that which we observe for dimethylhafnocene. The shorter distances are comparable to our values.

The cyclopentadienyl groups of dimethylhafnocene and its hydrolysis product have geometries typical of this group in organometallic compounds. In both, the thermal motions of the ring are moderately large, but of reasonable orientation. The minor axes of all such thermal ellipsoids are oriented approximately along the Hf–C direction, and the major axes in most cases are consistent with a librational motion of the ring about the Hf–centroid vector. All rings are reasonably planar, maximum deviations of atomic positions from the best plane of the appropriate five carbon atoms being 0.009 Å for both Cp rings of dimethylhafnocene and 0.016 and 0.012 Å for those of μ-oxo-bis(methylhafnocene). Average C–C distances and C–C–C angles within the rings are 1.383 (11) Å and 108.0 (5)° for the parent compound and 1.380 (16) Å

and 108.0 (9)° for the dimer.

The most obvious measure of distortion from ideal tetrahedral geometry is the centroid–Hf–centroid' angle. This parameter has a value of 132.1° in dimethylhafnocene and 128.5° in the dimer. Comparable values are 134° in $Cp_2HfC_4(C_6H_5)_4$, 129.5° in $(CH_2)_3(C_5H_4)_2HfCl_2$, and 121.0° in $(C_9H_7)_2Hf(CH_3)_2$.

Dimethylhafnocene is the archetypical alkyl hafnium cyclopentadienide compound and, as such, is of primary interest in the characterization of the hafnium–carbon σ bond. A very surprising result arising from this investigation is the nonequivalence of the two methyl groups of dimethylhafnocene. The two Hf–C(σ) distances differ by 0.064 Å, about six times the standard deviation of the difference, and thus are without a doubt significantly distinct. Both are longer than the Hf–C(σ) distance found in the oxo dimer, 2.295 (14) Å, although this difference is probably not significant for Hf–C(1). Figure 3 illustrates the crystal packing of dimethylhafnocene, in which there are no unusually short intermolecular interactions which might account for the observed

Table VI. Close Nonbonding Intramolecular Contacts in Dimethylhafnocene

Contact	Distance, Å	Contact	Distance, Å
C(1)–C(3)	3.20	C(2)–C(1)	3.46
C(1)–C(7)	3.26	C(2)–C(6)	3.11
C(1)–C(10)	3.26	C(2)–C(9)	3.11
C(1)–C(11)	3.14	C(2)–C(10)	3.44

discrepancy in Hf–methyl bond distances. Examination of the intramolecular methyl–Cp distances (Table VI) reveals closer contacts to the "long" methyl group, C(2), than to C(1), and a decrease in the Hf–methyl bond length would tend to further decrease these intramolecular contact distances.

The hypothesis that the Hf–C(σ) bond distance is quite sensitive to subtle effects is supported by other recent structural work. The Hf–methyl distance of 2.332 (12) Å in (indenyl)$_2$Hf(CH$_3$)$_2$ is longer than that found in its *isomorphous* Zr analogue,[5] while the polyhapto M–C distances exhibit the opposite (and expected) trend. These effects are understandable, as an examination of atomic radii indicates that Hf–C(σ) is actually a rather long, and thus presumably weak, σ bond. For the compound (CH$_2$)$_3$(C$_5$H$_4$)$_2$HfCl$_2$, a very good approximation to the observed length of the Hf–Cl σ bond may be obtained by addition of the hafnium metallic radius[18] and the chlorine covalent radius. The appropriate sum for the methylhafnium system is 2.21 Å, which is 0.1–0.2 Å shorter than the distances actually observed.

It has been known for some time that compounds containing carbon–zirconium or carbon–hafnium σ bonds are very susceptible to hydrolysis.[5–6,19,20] We have briefly reported that both (η^5-C$_5$H$_5$)$_2$Zr(CH$_3$)$_2$ and (η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$ appear to hydrolyze readily, giving new compounds containing M–O–M linkages, as evidenced by the infrared spectra of the products.[6] In the present study, (η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$ was found to undergo facile hydrolysis when a solution of this substance in a hydrocarbon solvent was exposed to the atmosphere for a period of 1–2 days.

The hydrolysis product was identified as μ-oxo-bis(methylhafnocene), [(η^5-C$_5$H$_5$)$_2$HfCH$_3$]$_2$O, on the basis of its infrared, proton NMR, and mass spectra, subsequent to the single-crystal x-ray diffraction study (vide supra). An infrared spectrum of the hydrolysis product exhibits an intense broad absorption between 760 and 790 cm^{-1}, which is assignable to a metal–oxygen stretching frequency and which is diagnostic for group 4A organometallic compounds containing a M–O–M linkage.[21–25] An absorption assignable to the remaining methyl substituent is also evident at 2900 cm^{-1}, and absorptions representative of a η^5-cyclopentadienyl ring are observed at 3100, 1430, 1005, and 820 cm^{-1}.

A proton NMR spectrum of the hydrolysis product, measured in C$_6$D$_6$, exhibits resonances at τ 9.85 and 4.22 due to methyl and cyclopentadienyl substituents, respectively. As might be expected, the methyl resonance in [(η^5-C$_5$H$_5$)$_2$HfCH$_3$]$_2$O is substantially deshielded compared to the corresponding resonance in (η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$ when measured in the same solvent, and even the cyclopentadienyl proton resonance appears at slightly lower field [τ 4.22 vs. τ 4.25 in (η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$].

The mass spectra of both (η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$ and [(η^5-C$_5$H$_5$)$_2$HfCH$_3$]$_2$O are summarized in Table VII, and both are in accord with the assigned structures. Neither organohafnium compound exhibits a molecular ion, although the base peak for each compound is observed at m/e 325 and 651, respectively, representing (M – CH$_3$)$^+$ in both instances. The next most intense peak in the spectrum of the hydrolysis product [(η^5-C$_5$H$_5$)$_2$HfCH$_3$]$_2$O is observed at m/e 635, representing the loss of 16 mass units (probably CH$_4$) from the ion of m/e 651, and this transition is supported by a metastable peak at m/e 617. Yet another peak at m/e 569

Table VII. Mass Spectral Data for (η^5-C$_5$H$_5$)Hf(CH$_3$)$_2$ and [(η^5-C$_5$H$_5$)$_2$HfCH$_3$]$_2$O^a

(η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$^{b}			[(η^5-C$_5$H$_5$)$_2$HfCH$_3$]$_2$O^c		
m/e	Intensity	Assignment	m/e	Intensity	Assignment
391	3		717	10	(C$_5$H$_5$)$_4$(C$_5$H$_6$)Hf$_2$-(CH$_3$)O$^+$
325	100	(C$_5$H$_5$)$_2$HfCH$_3$$^+$			
310	54	(C$_5$H$_5$)$_2$Hf$^+$	651	100	(C$_5$H$_5$)$_4$Hf$_2$(CH$_3$)O$^+$
284	16		635	54	(C$_5$H$_5$)$_3$C$_5$H$_4$Hf$_2$O$^+$
245	5	C$_5$H$_5$Hf$^+$	617		Metastable
180	1	Hf$^+$	569	45	(C$_5$H$_5$)(C$_5$H$_4$)$_2$Hf$_2$O$^+$
			543	13	

^{a} Ionizing voltage = 80 eV; sample temperature = 125 °C. ^{b} Cluster peaks are reported for ^{180}Hf; the measured spectrum had satisfactory isotopic distributions. ^{c} The isotopic pattern for two hafnium atoms per molecule was determined, and reported peaks are based on the peak for two ^{180}Hf atoms in each cluster.

represents the loss of 66 mass units (probably C$_5$H$_6$) from the ion of m/e 635.[26] Finally, a weak peak at m/e 717 is likely due to a recombination ion, and could correspond to [(C$_5$H$_5$)$_4$(C$_5$H$_6$)Hf$_2$(CH$_3$)O]$^+$. The lower mass region is generally uninformative except for a number of doubly charged ion peaks.

X-ray structural data for cyclopentadienyl compounds containing M–O–M units are scarce, the only previous reports being crystal structures of [Cp$_2$TiCl]$_2$O and [CpTiOCl]$_4$. The dimeric titanium complex[27] contains a linear oxo bridge with Ti–O distance 1.78 (3) Å, and the tetramer[28] contains nearly linear oxo bridges with an average Ti–O distance of 1.788 (7) Å.

Linear oxo bridges are considerably better characterized and more extensive in coordination chemistry,[29–31] particularly that of Fe(III).[29] Two coordination compounds of Ti(IV) have been structurally characterized which contain linear or near-linear oxo bridges.[32,33] Generally, these coordination complexes exhibit M–O bond lengths which are somewhat shorter than those observed for typical oxygen-donor ligands, and this effect is usually attributed to sp hybridization of the bridging oxygen atom and (d–p) π interactions with the metal. Our Hf–O distance is 1.941 (3) Å, and the bridging Hf–O–Hf angle is 173.9 (3)°, quite typical of the short, linear bonds of the coordination compounds. Subtraction of the difference in metallic radii[18] between Hf and Ti (0.118 Å) from our Hf–O distance yields 1.823 (3) Å, which agrees within experimental uncertainty with the 1.78 (3) Å in [Cp$_2$TiCl]$_2$O and is slightly longer than the more precise value of 1.788 (7) Å found in the tetrameric structure [CpTiOCl]$_4$. Our corrected M–O distance agrees precisely with the Ti–O distance found in the most precisely determined μ-oxo-titanium(IV) coordination complex,[33] [TiO$_2$(C$_7$H$_3$O$_4$N)(H$_2$O)]$_2$O^{5-}.

Registry No. [(η^5-C$_5$H$_5$)$_2$HfCH$_3$]$_2$O, 59493-08-2; (η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$, 37260-88-1.

Supplementary Material Available: A listing of structure factor amplitudes for (C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$ and [(C$_5$H$_5$)$_2$HfCH$_3$]$_2$O (34 pages). Ordering information is given on any current masthead page.

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Notes

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Carbonyl Hemochromes[1]

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Many hemoproteins combine with carbon monoxide to form well-defined and quite stable carbonyl complexes, which have characteristic electronic, infrared, and Mossbauer spectra.[2] For these reasons, the carbonyl is one of the most frequently prepared hemoprotein derivatives. All carbonyl hemes contain diamagnetic iron(II).

Few simple (nonprotein) iron porphyrin carbonyls (carbonyl hemochromes, containing six-coordinated iron(II)) have been systematically studied, except for the work by Caughey et al.[3,4] on the CO infrared stretching frequencies of several carbonyl hemochromes. A recent report by Collman et al.[5] describes some carbonyls of a "picket fence" heme.

We have prepared several carbonyl hemochromes and have measured their infrared and Mossbauer spectra. The results are reported here.

Experimental Section

The bis(morpholine), bis(pyrrolidine), and bis(piperidine) hemochromes of *meso*-tetra(*p*-anisidyl)porphinatoiron(II) (PMXPPFe·2L, L = morph, pyrr, pip) were prepared by reaction of the hemin chloride [PMXPPFeCl] with the neat hot amine, and the bis(pyridine) and bis(imidazole) hemochromes (L = py, Im) by displacement of piperidine from the bis(piperidine) hemochrome.[6] In all cases, except for imidazole, the hemochrome was recrystallized several times from the hot amine in order to remove any amine hydrochloride and all traces of the only slightly soluble μ-oxo contaminant, (PMXPPFe)₂O. The bis(imidazole) hemochrome was washed well with ether to remove excess imidazole.

For the preparation of the carbonylamine-*meso*-tetra(*p*-anisidyl)porphinatoiron(II) complexes, about 0.5 g of the bis(amine) hemochrome was added to about 50 ml of methylene chloride or benzene, saturated with carbon monoxide. (It is important to prevent the bis(amine) hemochrome in solution from coming into contact with oxygen as it is easily oxidized to the unreactive μ-oxo compound.)

Table I. Mössbauer and Infrared Data of Carbonyl Hemochromes at 298 K

Compd	$\nu_{CO},^a$ cm^{-1}	$\delta,^b$ mm/s	$\Delta,^c$ mm/s	$\Gamma,^d$ mm/s	N^e
PMXPPFe·morph·CO	1996	+0.49	0.55	0.36	0.90
PMXPPFe·pip·CO	1981	+0.47	0.49	0.30	1.64
PMXPPFe·py·CO	1978	+0.46	0.49	0.29	1.38
PMXPPFe·pyrr·CO	1982	+0.45	0.45	0.29	1.35
PMXPPFe·Im·CO	1966	+0.45	0.36	0.29	0.98

^{a} Average value of carbonyl stretching frequency determined for KBr pellet and Halocarbon oil mull samples; ±5 cm^{-1}. ^{b} Isomer shift relative to sodium nitroprusside; ±0.03 mm/s. ^{c} Quadrupole splitting; ±0.03 mm/s. ^{d} Line width at half-maximum. ^{e} Number of γ-ray counts under nonresonant conditions; ×10^6.

After 10–15 min of stirring under carbon monoxide, the solution was filtered, and, while bubbling carbon monoxide through the filtrate, it was reduced to about 10 ml by heating. Addition of pentane caused the formation of crystals, which were collected, washed with pentane, and dried at room temperature. Yields were nearly quantitative.

Infrared spectra were obtained on a Beckman IR-8 spectrophotometer with samples prepared in Halocarbon oil mulls and KBr pellets. Differences in CO stretching frequencies were less than 5 cm^{-1} for the two samples and only average values are reported.

Mössbauer spectra were obtained with a scanned-velocity spectrometer operating in the time mode and calibrated with sodium nitroprusside and ^{57}Fe foil. Spectra were fitted with a least-squares approximation assuming two Lorentzian line shapes of equal width. Estimated error limits on the isomer shift, δ, and quadrupole splitting, Δ, are ±0.03 mm/s. A Calcomp plotter was used to plot data.

Results and Discussion

The CO stretching frequency occurred as a single, sharp, strong peak in the 1965–1996-cm^{-1} range for the five carbonylaminetetraanisidylporphinatoiron(II) complexes investigated in this study (Table I). The frequency depended upon the amine and increased in the order imidazole < pyridine ~ pyrrolidine, piperidine < morpholine. (One sample of the imidazole complex had two peaks, at 1966 and 1927 cm^{-1}, but had a Mössbauer spectrum identical with that of a sample which showed only one peak, at 1966 cm^{-1}.) Imidazole is the strongest σ donor of these amines, which leads