Perhaps this is due to the larger AsO_4^{3-} ion relative to $\overline{PO}_4^{3-}$; note the substantial increase in cell volume (Table I). Obviously, it is the smaller ferrous ion ($r = 0.75$ Å) that allows the collapse of the seven-coordinated M(1) site in graftonite to six-coordination in $Fe_3(PO_4)_2$. The additional stability gained by a possible Fe(1)–Fe(1) interaction (indicated by the shorter bond distance) may also contribute to the lower coordination. [Our Mossbauer measurements of $Fe_3(PO_4)_2$ at 77°K do not show the presence of magnetic order.] It would be of interest to complete a detailed structural analysis of $Mn_3(PO_4)_2$ in order to elaborate upon this analysis.

Contribution from the Chemistry Department, Ohio University, Athens, Ohio 45701, and University of Houston, Houston, Texas 77004

Structural Studies of (π-C$_5$H$_5$)$_2$MX$_2$ Complexes and Their Derivatives. Structure of (1,1'-Trimethylene-π-dicyclopentadienyl)hafnium Dichloride

CARLOS H. SALDARRIAGA-MOLINA,[1] A. CLEARFIELD,* and IVAN BERNAL

(1,1'-Trimethylene-π-dicyclopentadiene)hafnium dichloride, $(CH_2)_3(C_5H_4)_2HfCl_2$, is orthorhombic, space group *Pbca*, and isomorphous with the corresponding zirconium compound. The unit cell dimensions are $a = 8.177$ (3) Å, $b = 13.916$ (4) Å, and $c = 22.425$ (9) Å, with $Z = 8$. The structure was determined from three-dimensional X-ray data (1797 independent reflections), obtained by means of an automated four-circle diffractometer, and refined anisotropically to an R of 0.029. The coordination about the hafnium atom is that of a distorted tetrahedron comprised of the chlorine atoms and the centroids of the π-cyclopentadienyl rings. The Cl–Hf–Cl bond angle is 95.87 (8)° and the centroid–Hf–centroid angle 129.5°. The Hf–Cl bond distances are 2.417 (3) and 2.429 (2) Å. These are slightly smaller than the corresponding bond distances in the zirconium complex and are in agreement with the sum of the Pauling radii. Distances from the hafnium atom to the ring centroids are 2.170 and 2.181 Å and the range of Hf–C distances is 2.459–2.501 Å. The carbon–carbon bond distances within the cyclopentadiene rings average 1.404 Å and range from 1.368 (17) to 1.438 (12) Å. These parameters not only establish the pentahapto nature of the metal–ring bonding but indicate that when the thermal motion of the rings is reduced by the constraints of the exocyclic bridge, the C–C bond lengths have a narrower range and calculate closer to the expected value of 1.41 Å.

Introduction

This study is a continuation of our research into the chemistry and stereochemistry of dicyclopentadienyl compounds of the group IVb transition elements. The study of the title substance was prompted by the following considerations.

(a) Previous studies by Davis and Bernal[2,3] and by Epstein and Bernal[4] have shown that the C–C bond lengths of the π-cyclopentadiene rings vary according to the degree of librational motion about the metal–ring centroid vector. In order to document this observation with additional data, we have undertaken a study of the series of compounds with formulas (π-C$_5$H$_5$)$_2$MCl$_2$ and (CH$_2$)$_3$(π-C$_5$H$_4$)$_2$MCl$_2$, where M = Ti, Zr, Hf. The object of the comparison is to demonstrate that in the latter series of compounds, where thermal motion is severly hindered by the aliphatic chain linking the π-C$_5$H$_4$ moieties, the C–C distances are more uniform. Inas-

much as there are no further changes in the two series, the conclusion that thermal motion is responsible for the large variations in C–C distances in the unbridged series would be unassailable, if experimentally substantiated by the structural results. The structure of (CH$_2$)$_3$(π-C$_5$H$_4$)$_2$TiCl$_2$ has already been determined by X-ray[2] and by neutron diffraction[4b] methods. The structure of (π-C$_5$H$_5$)$_2$TiCl$_2$ has been reported;[5] however, the refinement was apparently not carried to completion. We are currently redoing the X-ray structural analysis on an untwinned crystal of that substance.[6]

(b) Accurate studies of series of compounds like the group IVb cyclopentadienes and of homologous series of substances with larger and larger numbers of electrons in the d shells will be useful in deciding whether the so-called Ballhausen-Dahl[7] theory, the Alcock theory,[8] or some compromise between the two is the correct interpretation of the bonding in organometallics of the type (π-C$_5$H$_5$)$_2$MX$_2$.

(c) Finally, we were interested in establishing the effect of purity on the structural determination of hafnium com-

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* To whom correspondence should be addressed at Ohio University.

(1) This paper is one of a series based upon the Ph.D. thesis of C. H. S. presented to the Department of Chemistry, Ohio University, March 1974.

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pounds. It is a well-known fact that commercial hafnium is heavily contaminated with zirconium; thus, we wanted to find out the effect this would have on a structural study. The samples we used in our X-ray study were analyzed by neutron activation analysis[9] and this information was built into the structural refinement. The results are given below.

Experimental Section

Crystals of $(CH_2)_3(\pi\text{-}C_5H_4)_2HfCl_2$ suitable for X-ray diffraction work were provided by Dr. M. Hillman. They were shaped in the form of square antiprisms, approximately, with two opposite corners cut roughly halfway from the crystal centers. The crystal used in data collection had pale yellow coloration and the approximate dimensions of 0.17 × 0.34 × 0.15 mm parallel to the *a, b,* and *c* axes, respectively. Other crystal properties, such as the density, etc., are given in Table I.

A crystal was sealed in a capillary tube and mounted with the *b* axis approximately parallel to the goniometer θ axis. The diffractometer settings (crystal to counter and crystal to aperture distances, scan width, and scan rate, etc.) were described elsewhere.[10] The unit cell dimensions were obtained with a CAD-4 automated four-circle diffractometer (Enraf-Nonius). Twenty-five reflections at high and moderate Bragg angles were scanned at both ±2θ using a graphite monochromator and 4° takeoff angle. The Bragg angles were accurately determined by use of program DETCELL[11] which automatically compensates for wavelength dispersion (Mo Kα). Then the cell dimensions were obtained from a least-squares calculation using θ_1 values and $\lambda_{Mo\,K\alpha_1}$ 0.70926 Å.

Intensity data were collected by the θ-2θ scan technique out to a value of $2\theta_{max} = 70°$ with Mo Kα (λ 0.7107 Å) radiation. Three intensity control reflections, remeasured every time a batch of 32 reflections was collected, showed a random fluctuation about the average with a maximum deviation of about 4%. Their intensities were subsequently used to place all reflections on a common scale. A total of 7245 independent reflections were scanned in the +h+k+l octant of which 1797 had intensities equal to or greater than 3σ where $\sigma(I)$ = [total counts + background counts]$^{1/2}$ and were considered to be observed. The total scan count (T_0) and the background counts (B_1, B_2) were combined to yield a set of integrated intensities of the type given by the equation

$$I = T_0 - 2(B_1 + B_2)$$

These intensities were then corrected for the usual Lorentz and polarization effects.

As is common in hafnium compounds, zirconium was found isomorphously substituting the heavy atom in (1,1'-trimethylenedicyclopentadienyl)hafnium dichloride. The Zr:Hf ratio was found to be 0.141 which is equivalent to 12.3% substitution of zirconium for hafnium.[9] Consequently, the density given in Table I was calculated taking into account this substitution, which gives an effective molecular weight for the complex of 408.9, as opposed to a value of 419.6 if the heavy atom were 100% Hf. The measured density, determined by suspension of a single crystal in a mercuric nitrate solution, agreed quite well with the calculated one.

Another quantity affected by the presence of zirconium was the linear absorption coefficient, μ, the calculation of which requires a combined absorption coefficient. In the present case the mass fraction of hafnium is 0.383 and that of zirconium 0.027 so that the mass absorption coefficient for the complex is 37.75 cm²/g. Thus μr is found to have values of 0.683, 1.355, and 0.602 along the *a, b,* and *c* axes, respectively. Accordingly, the primary X-ray beam would almost be cut in half when traversing the crystal along the longest dimension. So, an absorption correction was applied using the program of Ahmed and Singh.[12] This program calculates a factor (the transmission factor, T) to be used in the adjustment of the integrated intensity of every reflection by means of the *m*-point gaussian integration formula. In the calculation $M_1, M_2,$ and M_3 were given values of 6, 8, and 12, respectively, and the crystal dimensions used were those given before. Absorption factors (reciprocals of

Table I. Crystal Data

Chemical formula	$(CH_2)_3(C_5H_4)_2HfCl_2$
Mol wt^a	408.9
Crystal system	Orthorhombic
Cell dimensions	$a = 8.177$ (3) Å
	$b = 13.916$ (4)
	$c = 22.425$ (9)
Cell volume	2551.8 Å³
Systematic absences	$0kl$ for $k \neq 2n$
	$h0l$ for $l \neq 2n$
	$hk0$ for $h \neq 2n$
Space group	*Pbca*
d_{obsd}	2.09 g cm^{-3}
d_{calcd}	2.125 g cm^{-3}
Z	8
μ(Mo Kα)^a	80.3 cm^{-1}
F(000)	1584 e

^{a} See text.

the transmission factors) were found to have values in the range of from 2.085 to 2.522.

Solution and Refinement of the Structure

Since this and the similar zirconium complex are isomorphous, the positional parameters found previously for zirconium and all the non-hydrogen atoms[10] provided the starting set for a successful refinement of the coordinates of hafnium and all the chlorine and carbon atoms, respectively, in the structure of the hafnium complex. Three separate refinements were carried out.[13] In the first the data were corrected for Lorentz and polarization effects but not for absorption and the metal atom scattering factor was not corrected for the presence of zirconium. In the second refinement a combined scattering factor allowing for the presence of 12.3% Zr was substituted for the uncorrected metal atom scattering factor. The final refinement was one in which both the combined scattering curve and absorption corrections were used. The function minimized in the analysis of this structure was $\Sigma w(|F_o| - |F_c|)^2$ with the weights, w, given by the expression

$$w = 1/\{1 + [(|F_o| - 125.0)/45.0]^2\}$$

Three agreement indices were used to assess the course of the refinement. These were $R(F) = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, and goodness of fit = $[\Sigma w(\Delta |F|)^2/(M - N)]^{1/2}$ where M is the number of observed reflections and N the number of variables refined. The final agreement indices were as follows.

	$R(F)$	$R_w(F)$	G of F
First	0.032	0.035	0.028
Second	0.030	0.031	0.024
Third	0.029	0.029	0.022

Thermal parameters were refined anisotropically as this was indicated to be necessary from the appearance of difference maps. Anisotropic refinement lowered $R(F)$ from 0.061 to 0.036 and from 0.050 to 0.031 for the first and third refinements, respectively. Hydrogen atoms were found on the difference maps after the anisotropic refinement but were placed ideally in the structure.[14] They were assigned isotropic temperature factors one unit higher than the atom to which they were bonded. The hydrogen positional and thermal parameters were held fixed in subsequent refinement cycles; however their inclusion lowered the agreement indices to their final values. The shifts in positional and thermal parameters were all less than 0.1 the esd values at the conclusion of the refinements.

A final difference Fourier map, calculated for the third refinement, showed residual density ranging from a maximum of about +1.5 to a minimum of about −1.5 e Å^{-3} associated with the hafnium atom. These extrema, however, were distributed in patterns characteristic of residual anisotropic motion and/or anisotropic absorption[15] which were not completely accounted for by the anisotropic temperature factors and the absorption correction applied. Smaller peaks

(9) The neutron activation analysis was carried out, at Brookhaven National Laboratory, by Dr. M. Hillman.

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(13) The programs used in this work were those of F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, "NRC Crystallographic Programs for the IBM/360," Division of Pure Physics, National Research Council, Ottawa, Canada, 1968.

(14) A. Stanislowski and B. Frenz, "Program Hydrogen," Texas A&M University Crystallographic Library, College Station, Tex.

(15) M. J. Buerger, "Crystal Structure Analysis," Wiley, New York, N. Y., 1960, p 608.

Table II. Fractional Coordinates and Isotropic Temperature Factors for Nonhydrogen Atoms in $(CH_2)_3(C_5H_4)_2HfCl_2$ (Absorption-Corrected Data)

Atom	x	y	z	B, Å²
Hf	0.12044 (2)	0.15742 (2)	0.11267 (1)	2.03
Cl(1)	0.0027 (3)	0.0285 (2)	0.1705 (1)	4.54
Cl(2)	0.2909 (3)	0.0553 (2)	0.0509 (1)	3.77
C(1)	0.0518 (13)	0.3598 (6)	0.2105 (5)	4.26
C(2)	−0.0582 (14)	0.4077 (7)	0.1668 (5)	4.78
C(3)	−0.1803 (12)	0.3413 (8)	0.1365 (5)	4.76
C(4)	0.0074 (14)	0.2832 (7)	0.0474 (4)	4.58
C(5)	0.0159 (16)	0.2007 (9)	0.0131 (4)	5.54
C(6)	−0.0898 (14)	0.1340 (8)	0.0359 (5)	6.11
C(7)	−0.1716 (12)	0.1741 (7)	0.0845 (6)	4.72
C(8)	−0.1100 (11)	0.2700 (6)	0.0925 (4)	3.88
C(9)	0.1760 (11)	0.2883 (6)	0.1855 (4)	2.81
C(10)	0.2854 (10)	0.3023 (6)	0.1396 (4)	3.29
C(11)	0.3939 (10)	0.2231 (6)	0.1382 (4)	3.25
C(12)	0.3507 (10)	0.1597 (6)	0.1843 (4)	3.50
C(13)	0.2145 (13)	0.2006 (7)	0.2145 (4)	3.57

(<0.4 e Å⁻³) were also found randomly distributed throughout the map.

The scattering factors used for the nonhydrogen atoms were those of Hanson, *et al.*,[16] with the metal and chlorine values corrected for anomalous dispersion (real part only).[17] The hydrogen atom scattering factors used were those of Stewart, *et al.*[18]

Table II lists the final positional and isotropic temperature parameters for the nonhydrogen atoms as obtained from the third refinement. Table III contains the anisotropic temperature factors, and the hydrogen atom coordinates are presented in Table IV. The observed and calculated structure factors are compared in Table V (in microfilm edition only).

The final, absorption-corrected atomic coordinates were essentially the same as those obtained from the other two refinements. The differences observed were as follows: the esd's decreased slightly for refinements 1–3, bond distances and angles were the same to within two standard deviations (which means some changes of 0.02–0.03 Å in the C–C bond lengths), and the thermal parameters were about 1–5% higher on the average in the absorption-corrected data. The big change was therefore in the scale factor which was about two-thirds that of the corresponding scale factors for the non-absorption-corrected data.

Description of the Structure

The molecular structure of $(CH_2)_3(C_5H_4)_2HfCl_2$ is essentially the same as the structure of the corresponding titanium[2,4a] and zirconium[10] derivatives with small differences in some geometrical parameters due to the different size of the hafnium atom. The configuration of the molecule is shown in Figure 1 which also explains the labeling scheme used throughout the structure analysis. A stereoscopic drawing of the molecule is given in Figure 2. Both figures were made with the final positional and thermal parameters of the third refinement and suggest the relative magnitude and direction of the thermal motion of the atoms.[19] Hydrogen atoms were included in the diagrams as spheres of arbitrarily chosen size (radius of 0.10 Å).

Table VI is a list of bonds and angles about the hafnium atom while Table VII shows the geometrical parameters of the 1,1'-trimethylenedicyclopentadienyl group. Except for the structure of tetracyclopentadienylhafnium,[20] no X-ray data are at present available in the literature on hafnium complexes similar to $(CH_2)_3(C_5H_4)_2HfCl_2$. Therefore, a
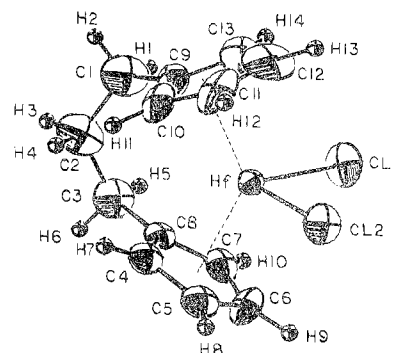

Figure 1. Configuration of the (1,1'-trimethylenedicyclopentadienyl)hafnium dichloride molecule showing the numbering scheme used in the tables.

detailed comparison of geometrical parameters with similar compounds is not possible. The interatomic distances and angles found here, however, agree well with the scanty geometrical data available.

The two Hf–Cl bond distances given in Table VI have a mean value of 2.423 (6) Å which is slightly lower than the average Zr–Cl distance of 2.441 (10) Å in the corresponding zirconium complex. This is most probably due to lanthanide contraction effects which almost exactly compensate for the expected difference of about 0.2 Å between the ionic radii of Hf^{4+} and Zr^{4+} and result in almost identical radii for the two ions.[21] In fact, if a constant covalent radius for chlorine is subtracted form the average metal–chlorine bond lengths in the zirconium and hafnium complexes, it is seen that the heavier element gives a slightly but significantly smaller radius. It is also interesting to note that Pauling's[22] metallic radii for zirconium and hafnium are 1.454 and 1.442 Å, respectively, and that if the covalent radius of chlorine (0.99 Å) is added to those two, a single-bond distance of 2.44 Å would be predicted for the Zr–Cl bond and a distance of 2.43 Å for the Hf–Cl bond in agreement with our structural results.

As in the zirconium complex molecule, all metal to aromatic carbon distances in $(CH_2)_3(C_5H_4)_2HfCl_2$ fall in a narrow range (2.459–2.501 Å) establishing a π or pentahapto type of bonding of the five-membered rings to the hafnium atom. The average Hf–C distance is 2.482 (4) Å and may be compared to the mean value of 2.50 Å found by Kulishov, Bokii, and Struchkov[20] between similar atomic centers in tetracyclopentadienylhafnium, $(C_5H_5)_4Hf$, where two of the five-membered rings are bonded to the metal in the penta-hapto mode and the other two have only one ring carbon atom close to the hafnium atom, making a bond of the (monohapto) σ type.

As is the case with the zirconium complex, so too with $(CH_2)_3(\pi-C_5H_4)_2HfCl_2$ the coordination about the metal atom is that of a distorted tetrahedron. The mean planes through chlorine–hafnium–chlorine and ring centroid(1)–hafnium–ring centroid(2), given by eq 1 and 2, respectively,

$$-0.7426X - 0.0815Y - 0.6647Z + 2.5928 = 0 \tag{1}$$

$$0.6648X + 0.0943Y - 0.7410Z + 1.0104 = 0 \tag{2}$$

are perpendicular to each other with the first bisecting the angle between the second group of positions and *vice versa*. This is seen to be the case from the distances of Cl(1) and Cl(2)

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Table III. Anisotropic Temperature Factor Coefficients (×10⁴) for Nonhydrogen Atoms in $(CH_2)_3(C_5H_4)_2HfCl_2$ (Absorption-Corrected Data)[a]

Atom	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Hf	74.7 (3)	24.0 (1)	11.5 (1)	−3.3 (6)	−4.4 (4)	−1.4 (2)
Cl(1)	203 (5)	47 (1)	27 (1)	−82 (4)	25 (3)	11 (2)
Cl(2)	149 (4)	49 (1)	20 (1)	38 (4)	8 (2)	−18 (1)
C(1)	174 (16)	43 (6)	28 (2)	2 (15)	−3 (11)	−30 (6)
C(2)	169 (17)	54 (6)	32 (3)	38 (17)	30 (13)	−8 (7)
C(3)	146 (14)	57 (5)	33 (3)	68 (19)	−6 (10)	−28 (7)
C(4)	207 (20)	54 (5)	20 (2)	69 (18)	−28 (11)	13 (6)
C(5)	252 (25)	100 (9)	14 (2)	110 (24)	−54 (12)	−11 (7)
C(6)	205 (23)	80 (8)	40 (3)	95 (20)	−108 (15)	−61 (8)
C(7)	126 (14)	51 (6)	43 (3)	18 (15)	−60 (12)	−1 (7)
C(8)	117 (13)	40 (4)	23 (2)	53 (15)	−28 (9)	−8 (4)
C(9)	124 (13)	37 (4)	16 (2)	−4 (12)	−1 (7)	−12 (4)
C(10)	93 (12)	35 (4)	24 (2)	−38 (12)	−2 (8)	−3 (5)
C(11)	82 (11)	49 (4)	23 (2)	−28 (13)	−8 (9)	−22 (5)
C(12)	157 (15)	35 (3)	23 (2)	19 (16)	−50 (8)	−3 (6)
C(13)	187 (18)	49 (5)	13 (2)	−50 (16)	−23 (9)	−1 (5)

[a] Temperature factors are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.
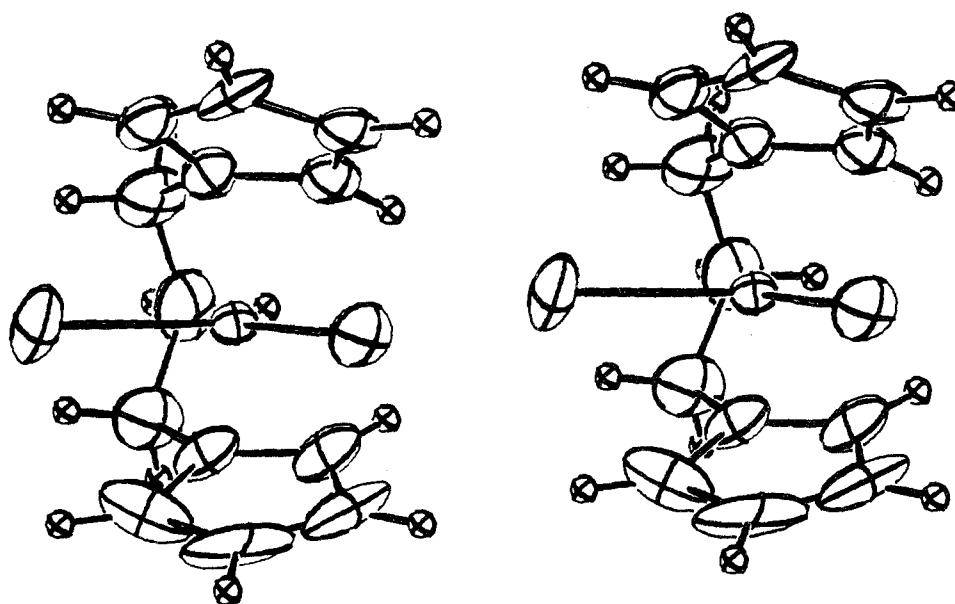
Figure 2. Stereoscopic view of $(CH_2)_3(C_5H_4)_2HfCl_2$. Thermal ellipsoids are at the 50% probability level.

Table IV. Hydrogen Atom Positional Parameters and Assumed Temperature Factors (Absorption-Corrected Data)

Atom	x	y	z	B, Å²
H(1)	−0.0182	0.3252	0.2382	5.10
H(2)	0.1089	0.4073	0.2332	5.10
H(3)	0.0090	0.4390	0.1368	5.45
H(4)	−0.1172	0.4599	0.1867	5.45
H(5)	−0.2576	0.3802	0.1150	5.88
H(6)	−0.2357	0.3074	0.1667	5.88
H(7)	0.0712	0.3413	0.0415	5.62
H(8)	0.0844	0.1916	−0.0207	6.62
H(9)	−0.1058	0.0699	0.0195	7.30
H(10)	−0.2537	0.1411	0.1117	5.74
H(11)	0.2874	0.3543	0.1109	4.14
H(12)	0.4822	0.2134	0.1099	4.23
H(13)	0.4045	0.1012	0.1947	4.60
H(14)	0.1596	0.1728	0.2483	4.51

Table VI. Interatomic Distances and Angles about the Hafnium Atom

(a) Bond Distances, Å

Hf–Cl(1)	2.417 (3)	Hf–Cl(2)	2.429 (2)
Hf–R(1)[a]	2.170	Hf–R(2)	2.181
Hf–C(4)	2.464 (10)	Hf–C(9)	2.489 (8)
Hf–C(5)	2.467 (10)	Hf–C(10)	2.501 (8)
Hf–C(6)	2.459 (10)	Hf–C(11)	2.486 (8)
Hf–C(7)	2.488 (10)	Hf–C(12)	2.479 (8)
Hf–C(8)	2.496 (9)	Hf–C(13)	2.486 (8)

Av Hf–C { ring 1	2.475 (7)[b]
ring 2	2.488 (4)
both rings	2.482 (4)

(b) Bond Angles, Deg

Cl(1)–Hf–Cl(2)	95.87 (8)	R(1)–Hf–R(2)	129.5
Cl(1)–Hf–R(2)	107.3	Cl(2)–Hf–R(1)	106.1
Cl(1)–Hf–R(2)	106.4	Cl(2)–Hf–R(2)	106.6

(1.773 and 1.823 Å, respectively) to the plane formed by the two ring centroids and the heavy atom and from the separation of the ring centroids with respect to the Cl–Hf–Cl plane. The last two are 1.960 Å for the centroid of the ring formed by C(4), C(5), C(6), C(7), and C(8) (ring 1) and 1.975 Å for the centroid of the ring formed by C(9), C(10), C(11), C(12) and C(13) (ring 2). The average separation of a chlorine atom from the centroid–metal–controid plane is slightly smaller in the hafnium complex (1.798 Å) than in the zirconium complex (1.827 Å) but substantially larger

[a] R(1) and R(2) are the two ring centroids. [b] Esd's of the average were calculated as $[\Sigma(X - \bar{X})^2/n(n - 1)]^{1/2}$, where n is the number of observations.

than in the similar titanium complex (1.729 Å).[2,10] A similar situation is found with the corresponding angles.

Carbon–carbon distances in the cyclopentadienyl groups range from 1.368 (17) to 1.438 (12) Å in ring 1 and from 1.379 (12) to 1.426 (13) Å in ring 2 (Table VII). The respective mean values are 1.399 (12) and 1.409 (8) Å. Both rings are exact pentagons with all the atoms, including the

Table VII. Bonds and Angles of the [(CH$_2$)$_3$(C$_5$H$_4$)$_2$] Group in the Hafnium Complex

(a) Bond Distances in Trimethylene Group, Å

| C(1)–C(2) | 1.490 (15) | C(1)–C(9) | 1.532 (13) |
| C(2)–C(3) | 1.522 (15) | C(3)–C(8) | 1.514 (13) |

(b) Bond Distances in Rings, Å

C(4)–C(5)	1.384 (15)	C(9)–C(10)	1.379 (12)
C(5)–C(6)	1.368 (17)	C(10)–C(11)	1.415 (12)
C(6)–C(7)	1.397 (16)	C(11)–C(12)	1.404 (12)
C(7)–C(8)	1.438 (12)	C(12)–C(13)	1.426 (13)
C(4)–C(8)	1.409 (14)	C(9)–C(13)	1.420 (12)

Av C–C { ring 1   1.399 (12)
        { ring 2   1.409 (8)

(c) Interatomic Angles in Trimethylene Group, Deg

| C(9)–C(1)–C(2) | 116.8 (8) | C(2)–C(3)–C(8) | 116.0 (8) |
| C(1)–C(2)–C(3) | 114.9 (9) | | |

| C(1)–C(9)–C(10) | 130.0 (8) | C(3)–C(8)–C(4) | 130.0 (8) |
| C(1)–C(9)–C(13) | 122.5 (8) | C(3)–C(8)–C(7) | 123.8 (8) |

(d) Bonding Angles in Cyclopentadienyl Rings, Deg

C(4)–C(5)–C(6)	108.9 (10)	C(9)–C(10)–C(11)	108.3 (7)
C(5)–C(6)–C(7)	109.0 (10)	C(10)–C(11)–C(12)	108.5 (7)
C(6)–C(7)–C(8)	107.4 (9)	C(11)–C(12)–C(13)	107.2 (7)
C(4)–C(8)–C(7)	105.7 (8)	C(9)–C(13)–C(12)	107.4 (8)
C(5)–C(4)–C(8)	109.0 (9)	C(10)–C(9)–C(13)	108.7 (7)

Av C–C–C { ring 1   108.0 (6)
          { ring 2   108.0 (4)

hydrogen atoms, lying in a plane. (Hydrogen atoms were originally calculated to lie in the plane.) Ring 1 may be described by eq 3 and ring 2 by eq 4, with indices of planari-

$$-0.7135X + 0.3501Y - 0.6069Z - 0.6977 = 0 \qquad (3)$$

$$-0.6176X - 0.4833Y - 0.6205Z + 5.4185 = 0 \qquad (4)$$

ty,[23] χ^2, of 1.445 and 0.949, respectively. The dihedral angle between the two five-membered rings is 49.4°, and as in the previous structure this angle is approximately bisected by the chlorine–metal–chlorine plane.[10] The latter makes angles of 24.4 and 25.2° with rings 1 and 2, respectively. As may be seen in Figure 3, none of the ten aromatic carbons deviate from their corresponding plane by more than 0.005 (7) Å, while the hydrogen atoms are all in the planes within about 0.02 Å. Atoms C(1) and C(3), on the other hand, are out of their respective planes by an average distance of 0.173 Å toward the hafnium atom, indicating again some degree of strain on the exocyclic chain.

The average trimethylene carbon to ring carbon distance is 1.523 (9) Å with an average angle of 126.1 (2)°. The interatomic distances between the trimethylene carbons average 1.506 (16) Å and the interatomic angles are again deformed (average 115.9 (6)°) with respect to tetrahedral angles, as was found in the corresponding zirconium complex.

A packing diagram of the hafnium-complex molecules is presented in Figure 4 where only the nonhydrogen atoms are shown for the sake of clarity. As may be seen in Table VIII, which gives a list of the shortest intra- and intermolecular distances about the hafnium and the two chlorine atoms, there are no unusually short interatomic contacts in the structure.

Conclusions

From the preceding description of the structures of (1,1'-trimethylenedicyclopentadienyl)titanium,[2] -zirconium,[10] and -hafnium dichlorides, it may be concluded that the molecular configurations of the three compounds are almost identical despite the fact that the first crystallizes in a mono-
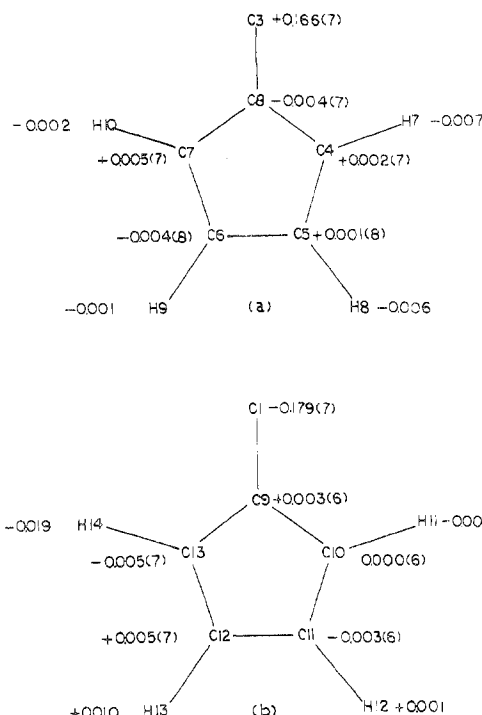
(23) D. M. Blow, *Acta Crystallogr.*, **13**, 168 (1960).

Figure 3. Displacements (in angstroms) of atoms from the best-fit mean plane through the cyclopentadiene rings: (a) ring 1; (b) ring 2. The esd's are given in parentheses.
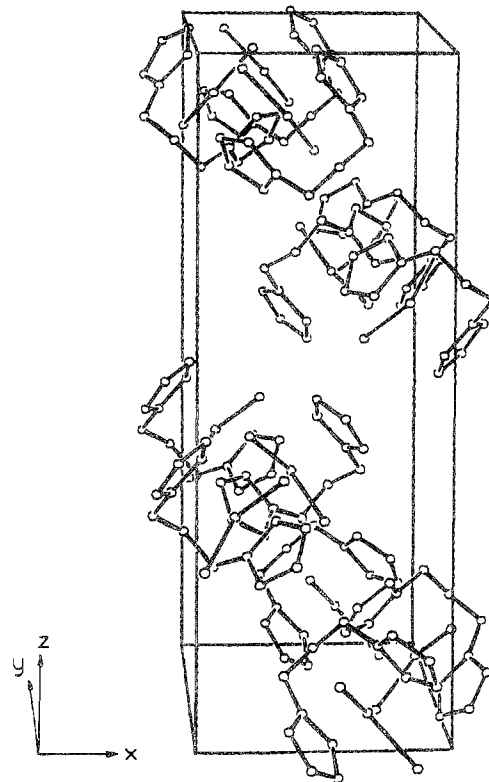

Figure 4. View of unit cell contents of (CH$_2$)$_3$(C$_5$H$_4$)$_2$HfCl$_2$ showing packing of molecules.

clinic system and the last two in orthorhombic systems. All three group IVb transition metal complexes consist of a metal atom surrounded by four ligands in approximately tetrahedral coordination. In all cases, the apices of the tetrahedra are the two cyclopentadienyl ring centroids and the two chlorine atoms, the first two being formally bound to the heavy atom in a pentahapto or π mode.

Table VIII. Nonbonded Intra- and Intermolecular Contacts (Å) Less Than 3.6 Å about the Hafnium and Chlorine Atoms

(a) Intramolecular Contacts

Hf–H(7)	3.03	Hf–H(11)	3.08
Hf–H(8)	3.04	Hf–H(12)	3.06
Hf–H(9)	3.02	Hf–H(13)	3.05
Hf–H(10)	3.07	Hf–H(14)	3.06
Cl(1)–Cl(2)	3.60	Cl(2)–C(5)	3.15
Cl(1)–C(6)	3.45	Cl(2)–C(6)	3.33
Cl(1)–C(7)	3.14	Cl(2)–C(11)	3.16
Cl(1)–C(12)	3.40	Cl(2)–C(12)	3.36
Cl(1)–C(13)	3.12	Cl(2)–H(8)	3.01
Cl(1)–H(10)	2.99	Cl(2)–H(9)	3.32
Cl(1)–H(13)	3.47	Cl(2)–H(12)	3.02
Cl(1)–H(14)	2.97	Cl(2)–H(13)	3.38
Cl(1)–H(9)	3.52		

(b) Intermolecular Contacts about Cl(1) and Cl(2)

Cl(1)–H(5)	3.14	000 3[a]
Cl(1)–H(11)	3.22	000 3
Cl(1)–H(1)	3.48	100 2
Cl(1)–H(4)	3.48	100 2
Cl(1)–H(2)	2.92	000 2
Cl(1)–H(3)	3.32	000 4
Cl(1)–H(4)	3.92	000 4
Cl(2)–H(9)	2.83	100 1
Cl(2)–H(7)	3.42	100 5
Cl(2)–H(3)	3.03	000 3
Cl(2)–H(7)	3.22	000 3
Cl(2)–H(11)	3.18	000 3

[a] The notation 000 3 indicates that the Cl atom is in symmetry position 3 with no cell translations. The symmetry positions 1–5 are respectively x, y, z; $x, 1/2 + y, 1/2 - z$; $1/2 - x, 1/2 + y, z$; $1/2 + x, y, 1/2 - z$; $1/2 + x, 1/2 - y, z$.

As evidenced by the interatomic angles between the bridging chain carbons and by the separations of the carbon atoms exterior and closest to the rings from the best-fit mean planes through the two sets of ring atoms, there is a considerable amount of strain in the $[(CH_2)_3(C_5H_4)_2]$ group brought about by the inclusion of a metal atom of size larger than what could normally be accommodated in an unconstrained system. This strain is seen to be relieved in the order Zr, Hf, Ti, wherein the metal atom covalent radii decrease. Other geometrical parameters involving the heavy-atom coordinates (Table IX) are also seen to follow this trend.

Table IX. Geometrical Parameters of 1,1′-Trimethylenedicyclopentadienyldichloro Complexes of the Group IVb Transition Metals

	Ti	Zr	Hf
M–Cl, Å	2.368 (2)	2.441 (10)	2.423 (6)
M–R,[a] Å	2.061	2.193	2.176
M–C(ring), Å	2.381 (5)	2.494 (4)	2.482 (4)
C–C(ring), Å	1.399 (5)	1.395 (5)	1.404 (7)
C–C(chain), Å	1.508 (5)	1.494 (9)	1.506 (16)
C–C(chain-ring), Å	1.495 (5)	1.503 (6)	1.523 (9)
Cl–M–Cl, deg	93.69 (5)	96.92 (7)	95.87 (8)
R–M–R, deg	132.6	129.5	129.5
Cl–M–R, deg	105.9	106.4	106.6
C–C–C(ring), deg	108.0 (3)	108.0 (6)	108.0 (3)
Dihedral angle (rings), deg	46.4	50.2	49.4

[a] R = ring centroid.

A comparison of interatomic distances between the cyclopentadienyl group carbons in these structures with similar ones in which the aromatic rings are not bridged[2-4] also reveals the expected result that the thermal motion of the rings is reduced on bridging, with the apparent consequence that the C–C bond lengths calculate longer and closer to the expected value of 1.41 Å.