Organometallics 1991, 10, 1592-1598

Understanding Electronic Effects in Organometallic Complexes. Influence of Methyl Substitution on Hafnocene Dihalides

Paul G. Gassman* and Charles H. Winter

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received December 7, 1990

A series of hafnocene dihalides was synthesized in which the total methyl substitution on the two cyclopentadienide moieties was 0, 3, 5, 6, 8, and 10. Each of these methyl-substituted hafnocene derivatives was analyzed by using X-ray photoelectron spectroscopy. The decrease in the Hf($4f_{7/2}$) binding energy per methyl group was 0.06 eV. The correlation of binding energies with methyl substitution for a series of hafnocene dichlorides was found to be linear (correlation coefficient of 0.991). Since steric effects are not linearly additive, the additivity of methyl substitution on the hafnocene dihalides established that methyl substitution on the cyclopentadienide rings of the hafnocene dihalides resulted in electron donation through the cyclopentadienide to the complexed transition metal. In order to ensure that the observed changes in binding energy with methyl substitution were not a result of major structural change due to steric interactions, a series of highly crystalline hafnocene dibromide complexes were subjected to single-crystal X-ray analysis. Hafnocene dibromide, 1,2,4-trimethylhafnocene dibromide, 1,2,3,4,5-pentamethylhafnocene dibromide, and 1,1′,2,2′,3,3′,4,4′,5,5′-decamethylhafnocene dibromide were found to have Cp–Hf–Cp angles of 130.5, 131.2, 130.3, and 129.8°, respectively. Hafnocene dibromide crystallized in the triclinic space group $P1$ with a = 7.986 (2) Å, b = 12.106 (2) Å, c = 12.555 (3) Å, and β = 79.75 (2)°. The calculated density was 2.746 g/cm^3 for four molecules in the unit cell at room temperature. The unweighted R factor was 0.028, and data were collected with the use of a variable-rate ω–2θ scan technique and graphite-monochromatized Mo Kα radiation. After Lorentz–polarization corrections, 3564 reflections with 2θ = 0–54° were observed for $[F_o^2 \geq 2\sigma(F_o^2)]$. 1,2,4-Trimethylhafnocene dibromide crystallized in the orthorhombic space group $Pna2_1$ with a = 13.562 (6) Å, b = 14.930 (4) Å, and c = 7.111 (2) Å. The calculated density was 2.355 g/cm^3 for four molecules in the unit cell at room temperature. The unweighted R factor was 0.036, and data were collected with the use of a variable-rate ω–2θ scan technique and graphite-monochromatized Mo Kα radiation. After Lorentz–polarization corrections, 1313 reflections with 2θ = 0–55° were observed for $[F_o^2 \geq 2\sigma(F_o^2)]$. 1,2,3,4,5-Pentamethylhafnocene dibromide crystallized in the orthorhombic space group $Pnam$ (a nonstandard setting of $Pnma$) with a = 9.078 (2) Å, b = 12.004 (2) Å, and c = 13.547 (7) Å. The calculated density was 2.266 g/cm^3 for four molecules in the unit cell at room temperature. The unweighted R factor was 0.024, and the data were collected with the use of a variable-rate ω–2θ scan technique and graphite-monochromatized Mo Kα radiation. After Lorentz–polarization corrections, 1436 reflections with 2θ = 0–54° were observed for $[F_o^2 \geq 2\sigma(F_o^2)]$. 1,1′,2,2′,3,3′,4,4′,5,5′-Decamethylhafnocene dibromide crystallized in the orthorhombic space group $Fmm2$ with a = 15.015 (7) Å, b = 16.787 (12) Å, and c = 8.277 (8) Å. The calculated density was 1.938 g/cm^3 for four molecules in the unit cell at room temperature. The unweighted R factor was 0.037, and the data were collected with the use of a variable-rate ω–2θ scan technique and graphite-monochromatized Mo Kα radiation. After Lorentz–polarization corrections, 1105 reflections with 2θ = 0–70° were observed for $[F_o^2 \geq 2\sigma(F_o^2)]$.

X-ray photoelectron spectroscopy has been shown to be a powerful tool for the evaluation of electronic effects in organometallic complexes.[1-3] We have previously shown that permethylation of the cyclopentadienide moiety of both "sandwich" complexes (ferrocenes,[1] ruthenocenes[2]) and "bent sandwich" complexes (titanocenes,[1] zirconocenes,[1] hafnocenes[1]) resulted in considerable electron donation to the complexed transition metal and, as a result, in decreased binding energies for the complexed transition metals. Of special interest was the question of whether these electronic changes represented a primary effect due to direct through-bond electron donations or whether the changes in binding energies were due to a secondary effect in which the major impact of methyl substitution was to change the overall structure through steric interactions which in turn would result in observable changes in the electronic character of the complexed transition metals. In order to distinguish between these two possible scenarios, we have prepared a series of methylated hafnocene dichloride, hafnocene dibromide, and hafnocene diiodide complexes and measured their binding energies by X-ray photoelectron spectroscopy. These results, combined with specific single-crystal X-ray structural determinations, support the contention that the changes in binding energies are due to direct through-bond electronic donation and not to changes in structure in these complexes.

Synthesis

A series of hafnocene dihalide derivatives (**1**–**6**, where X = Cl (**1a**–**6a**), Br (**1b**–**6b**), I (**1c**–**6c**)) was prepared with varying degrees of methyl substitution through the use of cyclopentadienide, 1,2,4-trimethylcyclopentadienide,[4] 1,2,3,4,5-pentamethylcyclopentadienide,[5] and combinations thereof as ligands. The hafnium complexes **1a**–**c**,[6] **3a**,[1,7] **6a**,[8] and **6c**[8] were previously reported in the literature and

---

[1] Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

[2] Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130.

[3] For related studies from our laboratory, see: Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* **1984**, *3*, 385. Gassman, P. G.; Macomber, D. W.; Willging, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380. Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228. Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875.

[4] Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793. Davies, A. G.; Lusztyk, E.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. 2*, **1982**, 729.

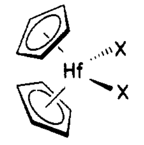
[5] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

[6] Druce, P. M.; Kingston, P. M.; Lappert, M. E.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.

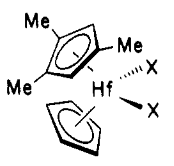
[7] Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriarity, K. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *293*, 51.

[8] Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

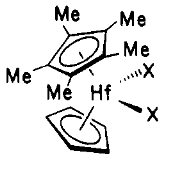
0276-7333/91/2310-1592$02.50/0



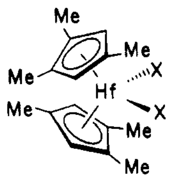
1a, X = Cl
b, X = Br
c, X = I



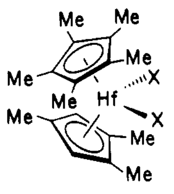
2a, X = Cl
b, X = Br
c, X = I



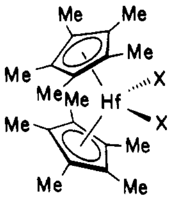
3a, X = Cl
b, X = Br
c, X = I



4a, X = Cl
b, X = Br
c, X = I

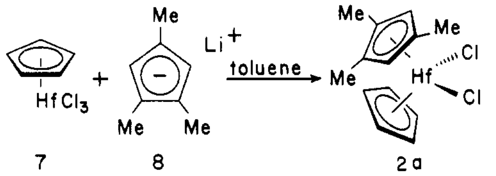


5a, X = Cl
b, X = Br
c, X = I

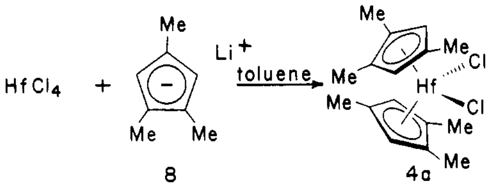


6a, X = Cl
b, X = Br
c, X = I

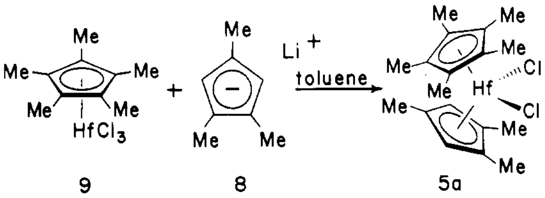
were prepared according to the published procedures. In order to obtain **2a**, cyclopentadienylhafnium trichloride



(**7**) was first prepared according to the literature procedure.[9] When **7** was treated with **8** in refluxing toluene, **2a** was obtained in 80% yield. The synthesis of **4a** was relatively straightforward. Hafnium tetrachloride was treated with **8** to give **4a** in 52% yield as white crystals.



The preparation of **5a** required the initial preparation of pentamethylcyclopentadienylhafnium trichloride (**9**).[10] Treatment of **9** with **8** gave **5a** in 48% yield as white crystals.



The dibromides, **1b**[6]–**6b**, and the diiodides, **1c**[6]–**6c** were prepared from the dichlorides, **1a**–**6a**, through treatment with boron tribromide and boron triiodide, respectively. The yields obtained for these reactions are shown in Table I.

X-ray Photoelectron Spectroscopic Studies of Methylated Hafnocene Dihalides

We previously reported the $Hf(4f_{7/2})$ binding energies for **1a**, **3a**, and **6a** to be 17.1, 16.8, and 16.5 eV, respectively.[1] The exact additivity of the change in binding energy vs the number of methyl groups was noted for these three compounds. It was this striking relationship that prompted us to carry out a much more detailed study of the influence of methyl substitution on the binding energies of the hafnocene dihalide complexes. Table II lists the binding energies for the methyl-substituted hafnocene dihalides. All of the samples were run on a polyethylene film, and all values were calibrated against the C(1s) binding energy of the polyethylene (284.6 eV) in order to correct for sample charging. As can be seen from Table II, variation of the halide had relatively little effect on the binding energies of the hafnocenes. However, methylation of the cyclopentadienide rings gives a systematic decrease in the $Hf(4f_{7/2})$ binding energies. Figure 1 shows a plot of the binding energies of **1a**–**6a** vs the number of methyl groups. As can be noted from this plot, the relationship is linear (correlation coefficient of 0.991). In general, steric effects increase exponentially while electronic effects are additive. Thus, the linear nature of the effect of methyl substitution as shown in Figure 1 provides strong evidence that the change in binding energy of the complexed hafnium is due to a through-bond electron donation, and not to a severe steric interaction of the methyl groups, which results in major structural changes.

Table I. Yields Obtained in the Preparation of 1b–6b and of 1c–6c through the Reaction of 1a–6a with Boron Tribromide and Boron Triiodide, Respectively

starting material	% yield of dibromide	% yield of diiodide	starting material	% yield of dibromide	% yield of diiodide
1a	60	48	**4a**	54	51
2a	65	50	**5a**	62	55
3a	86	76	**6a**	81	70

Table II. $Hf(4f_{7/2})$ Binding Energies of Hafnocenes

	binding energies (±0.1eV)		
compd	dichlorides	dibromides	diiodides
1a–c	17.1	17.0	16.9
2a–c	16.9	16.8	16.8
3a–c	16.8	16.7	16.8
4a–c	16.8	16.7	16.7
5a–c	16.6	16.5	16.6
6a–c	16.5	16.5	16.4

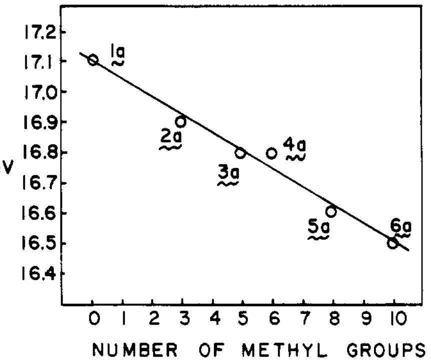


Figure 1. Binding energies for Hf $(4f_{7/2})$ vs the number of methyl groups on the cyclopentadienide rings.

X-ray Crystallographic Studies

The discussion provided above indicates that the linear nature of the relationship of methyl substitution to binding energy is electronic and not steric. In relation to this conclusion it was of interest to known what, if any, was the effect of the methyl substitution on the structures of the hafnocenes. Because of the excellent quality of their crystals, the hafnocene dibromide complexes were chosen for single-crystal X-ray determination. Table III lists the

---

(9) Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *148*, 35.

(10) Blenkers, J.; DeLiefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

Table III. Single-Crystal X-ray Data Collection Parameters for 1b–3b, and 6b

	1b	2b	3b	6b
formula	$C_{10}H_{10}Br_2Hf$	$C_{13}H_{16}Br_2Hf$	$C_{15}H_{20}Br_2Hf$	$C_{20}H_{30}Br_2Hf$
mol wt	468.50	510.58	538.63	608.76
cryst color, habit	off-white rods	light green rods	pale green cubes	light yellow rods
temp of data colln	ambient	ambient	ambient	ambient
cryst syst	triclinic	orthorhombic	orthohombic	orthorhombic
space group	$P\bar{1}$	$Pna2_1$	*Pnam* (nonstandard setting of *Pnma*)	*Fmm*2
cell dimens				
a, Å	7.986 (2)	13.562 (6)	9.078 (2)	15.036 (7)
b, Å	12.106 (2)	14.930 (4)	12.004 (2)	16.787 (6)
c, Å	12.555 (3)	7.11 (2)	13.547 (7)	8.265 (12)
β, deg	79.75 (2)			
V, Å^3	1133.0 (8)	1439.8 (7)	1578.7 (7)	2086.3 (5)
Z	4	4	4	4
d(calc), g/cm^3	2.746	2.355	2.266	1.938
scan method	variable ω–2θ	variable ω–2θ	variable ω–2θ	variable ω–2θ
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
monochromator	graphite crystal	graphite crystal	graphite crystal	graphite crystal
scan range, deg	0–54	0–55	0–54	0–70
scan rate, (deg min^{-1})	variable	variable	variable	variable
bckgd/scan time	0.5	0.5	0.5	0.5
no. of tot data	4948	1717	1797	1288
no. of obsd data				
$[F_o^2 \geq 2\sigma(F_o^2)]$	3564	1313	1436	1105
μ, cm^{-1}	160.72	126.57	115.50	87.51
R, R_w	0.028, 0.030	0.036, 0.041	0.024, 0.025	0.037, 0.045

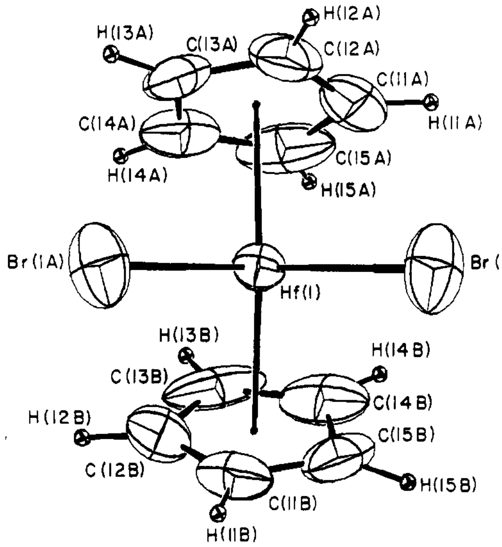


Figure 2. ORTEP drawing of hafnocene dibromide (**1b**).

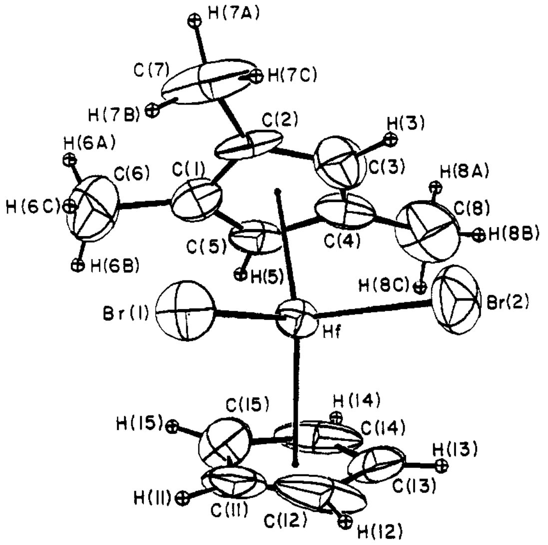


Figure 3. ORTEP drawing of 1,2,4-trimethylhafnocene dibromide (**2b**).

details of the data collection for **1b**–**3b** and **6b**. All four compounds gave X-ray data of very high quality.

Figure 2 shows an ORTEP drawing of **1b**. Table IV lists bond distances and bond angles for the two independent molecules in the unit cell. The cyclopentadienide ligands were planar to ±0.005 Å, and the ring carbon–carbon distances for the two molecules in the unit cell were 1.350 and 1.380 Å. The hafnium–carbon distances averaged 2.470 and 2.460 Å for the two independent molecules in the unit cell. The distance from the cyclopentadienide centroid to the hafnium was 2.173 and 2.175 Å. These values compare quite well with known hafnium–cyclopentadienide centroid values.[11] The cyclopentadienide centroid–hafnium–cyclopentadienide centroid values for the two distinct molecules in the unit cell were both 130.5°. The corresponding bromine–hafnium–bromine angles were 95.8 and 96.0°. The general agreement of the structural parameters of **1b** with those of other hafnocene derivatives[11] indicated that there was nothing structurally unusual about hafnocene dibromide and, as a result, it should serve as an excellent basis for comparison for **2b**, **3b**, and **6b**.

Figure 3 shows the ORTEP drawing of 1,2,4-trimethylhafnocene dibromide (**2b**). Table V lists the bond lengths and bond angles for **2b**. The cyclopentadienide ligands were planar to ±0.01 Å, and the ring carbon–carbon bond distances averaged 1.384 Å [$(CH_3)_3C_5H_2$] and 1.384 Å (C_5H_5). The distances from the 1,2,4-trimethylcyclopentadienide centroid and the cyclopentadienide centroid to the hafnium were 2.178 and 2.190 Å, respectively. The cyclopentadienide centroid–hafnium–1,2,4-trimethylcyclopentadienide centroid angle was 131.2°, and the bromine–hafnium–bromine angle was 95.8°. The structural parameters for **2b** compared quite well with those of **1b**.

---

(11) For selected examples, see: Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *Inorg. Chem.* **1974**, *13*, 2880. Fronczek, F. R.; Baker, E. C.; Sharp, P. R.; Raymond, K. N.; Alt, H. G.; Rausch, M. D. *Inorg. Chem.* **1976**, *15*, 2284. Stutte, B.; Bätzel, V.; Boese, R.; Schmid, G. *Chem. Ber.* **1978**, *111*, 1603. Tund, I.-C.; Hao, S.; Chang, J.-K.; Chen, S.-S. *K'o Hsueh Tung Pao (Chin. Ed.)* **1982**, *27*, 1436. Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

Table IV. Bond Lengths (Å) and Bond Angles (deg) for Hafnocene Dibromide (1b and 1b′)

Bond Lengths

Hf(1)–Br(1A)	2.581 (1)	Hf(2)–Br(2A)	2.580 (1)	C(11A)–C(12A)	1.390 (13)	C(21A)–C(22A)	1.341 (15)
Hf(1)–Br(1B)	2.578 (1)	Hf(2)–Br(2B)	2.580 (1)	C(12A)–C(13A)	1.383 (12)	C(22A)–C(23A)	1.315 (15)
Hf(1)–C(11A)	2.472 (8)	Hf(2)–C(21A)	2.483 (8)	C(13A)–C(14A)	1.342 (12)	C(23A)–C(24A)	1.387 (17)
Hf(1)–C(12A)	2.497 (7)	Hf(2)–C(22A)	2.471 (8)	C(14A)–C(15A)	1.394 (14)	C(24A)–C(25A)	1.363 (17)
Hf(1)–C(13A)	2.490 (7)	Hf(2)–C(23A)	2.447 (8)	C(15A)–C(11A)	1.399 (15)	C(25A)–C(21A)	1.332 (16)
Hf(1)–C(14A)	2.445 (8)	Hf(2)–C(24A)	2.437 (8)	C(11B)–C(12B)	1.370 (13)	C(21B)–C(22B)	1.351 (17)
Hf(1)–C(15A)	2.437 (8)	Hf(2)–C(25A)	2.467 (8)	C(12B)–C(13B)	1.373 (15)	C(22B)–C(23B)	1.352 (16)
Hf(1)–C(11B)	2.486 (7)	Hf(2)–C(21B)	2.478 (9)	C(13B)–C(14B)	1.398 (14)	C(23B)–C(24B)	1.324 (16)
Hf(1)–C(12B)	2.482 (8)	Hf(2)–C(22B)	2.475 (8)	C(14B)–C(15B)	1.367 (13)	C(24B)–C(25B)	1.359 (18)
Hf(1)–C(13B)	2.453 (7)	Hf(2)–C(23B)	2.475 (8)	C(15B)–C(11B)	1.376 (12)	C(25B)–C(21B)	1.376 (18)
Hf(1)–C(14B)	2.434 (7)	Hf(2)–C(24B)	2.439 (9)	Hf(1)–C(10A)[a]	2.171	Hf(2)–C(20A)[c]	2.178
Hf(1)–C(15B)	2.503 (7)	Hf(2)–C(25B)	2.430 (9)	Hf(1)–C(10B)[b]	2.177	Hf(2)–C(20B)[d]	2.174

Bond Angles

Br(1A)–Hf(1)–Br(1B)	95.83 (3)	Br(2A)–Hf(2)–Br(2B)	96.04 (3)
C(11A)–C(12A)–C(13A)	108.31 (84)	C(21A)–C(22A)–C(23A)	108.44 (104)
C(12A)–C(13A)–C(14A)	108.96 (83)	C(22A)–C(23A)–C(24A)	107.98 (101)
C(13A)–C(14A)–C(15A)	108.49 (90)	C(23A)–C(24A)–C(25A)	106.75 (99)
C(14A)–C(15A)–C(11A)	107.74 (82)	C(24A)–C(25A)–C(21A)	107.07 (110)
C(15A)–C(11A)–C(21A)	106.48 (89)	C(25A)–C(21A)–C(22A)	109.75 (99)
C(11B)–C(12B)–C(13B)	108.00 (88)	C(21B)–C(22B)–C(23B)	107.84 (111)
C(12B)–C(13B)–C(14B)	107.53 (78)	C(22B)–C(23B)–C(24B)	109.81 (113)
C(13B)–C(14B)–C(15B)	107.78 (90)	C(23B)–C(24B)–C(25B)	107.35 (119)
C(14B)–C(15B)–C(11B)	107.96 (87)	C(24B)–C(25B)–C(21B)	108.20 (113)
C(15B)–C(11B)–C(12B)	108.59 (83)	C(25B)–C(21B)–C(22B)	106.73 (112)
C(10A)[a]–Hf(1)–C(10B)[b]	130.5	C(20A)[c]–Hf(2)–C(20B)[d]	130.5

[a] Ring 1A centroid. [b] Ring 1B centroid. [c] Ring 2A centroid. [d] Ring 2B centroid.

Table V. Bond Lengths (Å) and Bond Angles (deg) for 1,2,4-Trimethylhafnocene Dibromide (2b)

Bond Lengths

Hf–Br(1)	2.577 (2)	C(1)–C(2)	1.385 (28)
Hf–Br(2)	2.589 (2)	C(2)–C(3)	1.391 (21)
Hf–C(1)	2.497 (16)	C(3)–C(4)	1.321 (25)
Hf–C(2)	2.578 (19)	C(4)–C(5)	1.416 (22)
Hf–C(3)	2.399 (25)	C(5)–C(1)	1.409 (23)
Hf–C(4)	2.452 (15)	C(11)–C(12)	1.281 (41)
Hf–C(5)	2.449 (13)	C(12)–C(13)	1.413 (34)
Hf–C(11)	2.490 (18)	C(13)–C(14)	1.360 (31)
Hf–C(12)	2.529 (20)	C(14)–C(15)	1.462 (29)
Hf–C(13)	2.510 (17)	C(15)–C(11)	1.402 (35)
Hf–C(14)	2.467 (16)	C(1)–C(6)	1.523 (26)
Hf–C(15)	2.432 (23)	C(2)–C(7)	1.530 (27)
Hf–C(0)[a]	2.178	C(4)–C(8)	1.527 (27)
Hf–C(10)[b]	2.190		

Bond Angles

Br(1)–Hf–Br(2)	95.81 (8)	C(3)–C(4)–C(8)	127.12 (191)
C(1)–C(2)–C(3)	105.85 (161)	C(5)–C(4)–C(8)	127.14 (136)
C(2)–C(3)–C(4)	112.40 (179)	C(11)–C(12)–C(13)	110.72 (199)
C(3)–C(4)–C(5)	105.74 (180)	C(12)–C(13)–C(14)	105.61 (204)
C(4)–C(5)–C(1)	108.12 (123)	C(13)–C(14)–C(15)	109.19 (193)
C(5)–C(1)–C(2)	106.92 (171)	C(14)–C(15)–C(11)	102.56 (203)
C(2)–C(1)–C(6)	125.65 (209)	C(15)–C(11)–C(12)	111.77 (206)
C(5)–C(1)–C(6)	127.22 (202)	C(0)[a]–Hf–C(10)[b]	131.2
C(1)–C(2)–C(7)	125.05 (245)		
C(3)–C(2)–C(7)	128.87 (228)		

[a] Trimethylcyclopentadienide centroid. [b] Cyclopentadienide centroid.

Table VI. Bond Lenths (Å) and Bond Angles (deg) for 1,2,3,4,5-Pentamethylhafnocene Dibromide (3b)

Bond Lengths

Hf–Br	2.575 (0)	C(11)–C(21)	1.498 (10)
Hf–C(1)	2.461 (6)	C(12)–C(22)	1.509 (6)
Hf–C(2)	2.469 (5)	C(13)–C(23)	1.500 (6)
Hf–C(3)	2.519 (4)	Hf–C(0)[a]	2.189
Hf–C(11)	2.529 (6)	Hf–C(10)[b]	2.205
Hf–C(12)	2.526 (4)		
Hf–C(13)	2.486 (4)		

Bond Angles

Br–Hf–Br	95.59 (3)	C(11)–C(12)–C(13)	107.88 (40)
C(1)–C(2)–C(3)	107.13 (52)	C(12)–C(13)–C(13)′	107.93 (25)
C(2)–C(3)–C(3)′	108.51 (35)	C(12)–C(11)–C(12)′	108.36 (56)
C(2)–C(1)–C(2)′	108.67 (62)	C(12)–C(11)–C(21)	125.71 (28)
C(0)[a]–Hf–C(10)[b]	130.3	C(11)–C(12)–C(22)	126.38 (46)
		C(13)–C(12)–C(22)	125.19 (46)
		C(12)–C(13)–C(23)	125.15 (43)
		C(13)–C(13)′–C(23)	126.06 (30)

[a] Cyclopentadienide centroid. [b] Pentamethylcyclopentadienide centroid.

Table VII. Bond Lengths (Å) and Bond Angles (deg) for 1,1′,2,2′,3,3′,4,4′,5,5′-Decamethylhafnocene Dibromide (6b)

Bond Lengths

Hf–Br	2.577 (1)	C(1)–C(4)	1.434 (22)
Hf–C(1)	2.505 (9)	C(2)–C(5)	1.510 (14)
Hf–C(2)	2.564 (7)	C(3)–C(6)	1.488 (28)
Hf–C(3)	2.578 (8)		

Bond Angles

Br–Hf–Br	93.80 (6)	C(2)–C(1)–C(4)	128.12 (53)
C(1)–C(2)–C(3)	107.31 (76)	C(1)–C(2)–C(5)	126.74 (151)
C(2)–C(3)–C(3)′	111.24 (63)	C(3)–C(2)–C(5)	125.43 (159)
C(2)–C(1)–C(2)′	102.65 (104)	C(2)–C(3)–C(6)	128.28 (144)
C(0)[a]–Hf–C(0)[a]	129.8	C(3)–C(3)′–C(6)	118.16 (112)

[a] Pentamethylcyclopentadienide centroid.

Thus, no structural distortion was seen to result from the three added methyl groups.

Figure 4 shows the ORTEP drawing of 1,2,3,4,5-pentamethylhafnocene dibromide (**3b**). Table VI lists the bond lengths and bond angles for **3b**. The cyclopentadienide ligands were staggered, and the methyl groups were arranged to minimize through-space methyl–bromine interactions. The cyclopentadienide ligands were planar to ±0.01 Å. The cyclopentadienide centroid–hafnium and 1,2,3,4,5-pentamethylcyclopentadienide centroid–hafnium distances were 2.189 and 2.205 Å, respectively. The carbon–carbon bond distances averaged 1.415 Å $[(CH_3)_5C_5]$ and 1.387 Å (C_5H_5). The cyclopentadienide centroid–hafnium–1,2,3,4,5-pentamethylcyclopentadienide centroid angle was 130.3°, and the bromine–hafnium–bromine angle was 95.6°. Within experimental error the skeletal structure of **3b** was the same as **1b** and **2b**.

Figure 5 shows the ORTEP drawing of 1,1′,2,2′,3,3′,4,4′,5,5′-decamethylhafnocene dibromide (**6b**). Table VII lists the bond lengths and bond angles for **6b**. For **6b**, the 1,2,3,4,5-pentamethylcyclopentadienide ligands

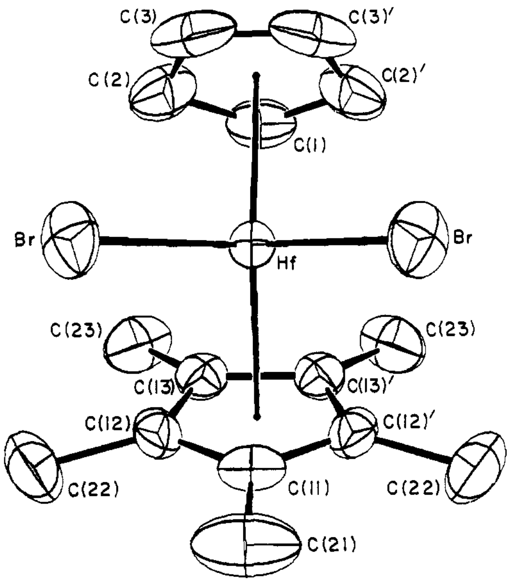


Figure 4. ORTEP drawing of 1,2,3,4,5-pentamethylhafnocene dibromide (**3b**). Hydrogens were omitted for clarity.

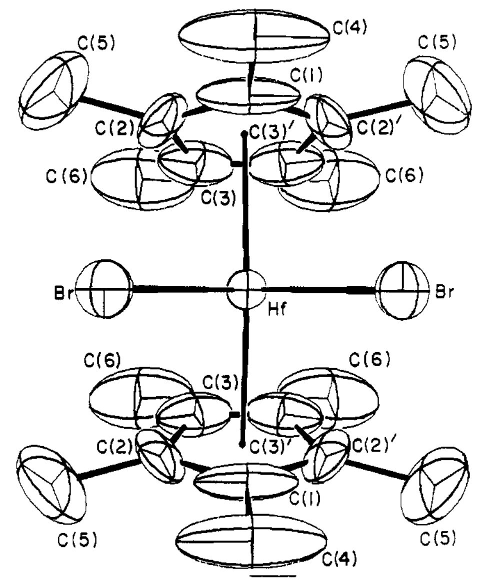


Figure 5. ORTEP drawing of 1,1′,2,2′,3,3′,4,4′,5,5′-decamethylhafnocene dibromide (**6b**). Hydrogens were omitted for clarity.

were eclipsed to minimize methyl–bromine nonbonded interactions. The cyclopentadienide rings were planar to ±0.01 Å, and the carbon–carbon bond distances averaged 1.342 Å. The 1,2,3,4,5-pentamethylcyclopentadienide centroid–hafnium distances averaged 2.281 Å. The 1,2,3,4,5-pentamethylcyclopentadienide centroid–hafnium–1,2,3,4,5-pentamethylcyclopentadienide centroid angle was 129.8°, and the bromine–hafnium–bromine angle was 93.8°. The single significant deviation of the skeletal structure of **6b** from that of the other three hafnocene dibromide structures was the cyclopentadienide centroid hafnium distance, which was 0.095 Å longer than the average of the corresponding distances in **1b**–**3b**. This probably is a result of the increased steric congestion that occurs when both rings are permethylated.

The addition of methyl groups to **1b** causes very little structural distortion. Table VIII gives a compilation of the critical features of **1b**–**3b** and **6b**. As is shown, the structural parameters for the four hafnocene dibromides are very similar. Hafnium–bromine distances, Cp–Hf–Cp angles, and Br–Hf–Br angles are virtually unchanged throughout the series. Only the cyclopentadienide centroid–hafnium distance increases throughout the series, and this increase is not linear with the number of methyl groups.

Table VIII. Comparison of Major Structural Features of 1b–3b and 6b

	1b	2b	3b	6b
Cp(centroid)–Hf,[a] Å	2.176	2.184	2.197	2.281
Hf–Br, Å	2.580	2.583	2.575	2.577
Cp–Hf–Cp, deg	130.5	131.2	130.3	129.8
Br–Hf–Br, deg	95.9	95.8	95.6	93.8

[a] When the cyclopentadienide ligands differed in substitution, the average of the cyclopentadienide–hafnium distances is shown.

It is of interest to note that the steric interactions do result in out-of-plane bending of the methyl groups attached to the cyclopentadienide ligands. For **2b**, the cyclopentadienide plane–methyl angles were as follows: C(6), -1.4° (toward hafnium); C(7), +4.3°; C(8), +5.0°. For **3b**: C(21), +2.9°; C(22), +7.6°; C(23), +7.8°. The largest out-of-plane distortions were noted for **6b**: C(4), +4.6°; C(5), +10.1°; C(6), +12.3°. It is apparent that a major factor in the relief of steric strain in these molecules is the out-of-plane bending of the methyl groups. It is important to recognize that this out-of-plane distortion has no detectable influence on the ability of the methyl groups to donate electron density to the cyclopentadienide ring, and through the ring to the complexed transition metal.

Discussion and Summary

As illustrated above, the influence of added methyl substitution on the hafnocene dihalides was to decrease the binding energy of the Hf($4f_{7/2}$) electrons of the complexed hafnium. Within detectable limits, this electron donation was primarily absorbed by the hafnium and was transmitted only slightly (if at all) to the halides, since the halide binding energies remained reasonably constant throughout each series.[12] Thus, the Cl(2p) binding energies for **1a**–**6a** were as follows: **1a**, 198.9 eV; **2a**, 198.8 eV; **3a**, 198.8 eV; **4a**, 199.0 eV; **5a**, 198.8 eV; **6a**, 198.8 eV.[13] For the bromide complexes, **1b**–**6b**, the corresponding Br (3d) binding energies were as follows: **1b**, 69.4 eV; **2b**, 69.3 eV; **3b**, 69.2 eV; **4b**, 69.2 eV; **5b**, 69.3 eV; **6b**, 69.2 eV.[13] The iodide complexes, **1c**–**6c**, gave the following I($3d_{5/2}$) binding energies: **1c**, 619.6 eV; **2c**, 619.4 eV; **3c**, 619.6 eV; **4c**, 619.5 eV; **5c**, 619.5 eV; **6c**, 619.4 eV.[13]

The linear relationship of Hf($4f_{7/2}$) binding energies to methyl substitution is only consistent with the methyl group being a significant electron-donating substituent. The single-crystal X-ray studies of the hafnocene dibromide complexes established that there is no linear systematic change of structure on increased methyl substitution. Thus, it is safe to conclude that the change which occurs in the electronic character of cyclopentadienide-complexed transition metals[1] on addition of methyl groups to the cyclopentadienide ring is due primarily to the linearly additive electron-donating ability of the methyl substituents.

Experimental Section

Proton magnetic resonance spectra were obtained on a Varian HFT-80 or Nicolet NT-300 spectrometer. Carbon magnetic resonance spectra were obtained on a Nicolet NT-300 spectrom-

---

(12) While a change of ~0.2 eV occurred in the halogen binding energies for each series of hafnocene dihalides as a result of increased methyl substitution from zero to ten, the overall change in binding energy is within the limits of experimental error. Since the same trend appears in all three series, it seems possible that a small degree of electron donation is passed through the hafnium to the halides.

(13) Experimental error is ±0.1 eV.

eter. Infrared spectra were obtained on a Beckman Model 4240 infrared spectrophotometer. Mass spectra were obtained an on AEI-MS 30 instrument in the electron impact mode at electron energies of either 20 or 70 eV. Melting points were determined on a Thomas-Hoover Uni-melt apparatus and are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Photoelectron spectra were obtained on a Physical Electronics Industries, Inc., ESCA-Auger-SIMS Model 548 system equipped with a Model 15-720 specimen introduction/reaction chamber, using Mg Kα radiation. The samples were run on polyethylene-coated aluminum chips. Each sample was calibrated against the C(1s) binding energy (284.6 eV) of polyethylene.

All reactions were run under an atmosphere of purified argon or nitrogen by using standard Schlenk techniques. Toluene and ether were distilled from sodium benzophenone ketyl just prior to use. Dichloromethane was distilled from calcium hydride. Hafnium tetrachloride and boron tribromide were purchased from Aldrich. Boron triiodide was used as received from Alfa. Complexes **1a–c**,[6] **6a**,[8] **6c**,[8] **7**,[9] and **9**[10] were prepared according to the literature procedures. 1,2,4-Trimethylcyclopentadiene was prepared by a literature method.[4]

1,2,4-Trimethylhafnocene Dichloride (2a). Into a 300-mL Schlenk flask, equipped with a stir bar and rubber septum was placed (η^5-cyclopentadienyl)hafnium trichloride (**7**) (2.70 g, 7.72 mmol), 1,2,4-trimethylcyclopentadienyllithium (**8**) (1.12 g, 9.80 mmol), and 60 mL of toluene in an inert atmosphere. The resultant mixture was refluxed for 24 h. The toluene was removed under reduced pressure to yield a light yellow solid. This solid was dissolved in 100 mL of methylene chloride and washed with 100 mL of 3 N hydrochloric acid. The methylene chloride layer was separated, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed to afford a light yellow solid. Recrystallization from methylene chloride/hexane afforded 2.59 g (80% yield) of a pure white solid: mp (sealed tube) 131–133 °C; IR (KBr) 3100, 3082, 2970, 2942, 2915, 1510, 1482, 1441, 1384, 1133, 1020, 1013, 894, 875, 842, 808, 607 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.20 (s, 5 H), 5.81 (s, 2 H), 2.19 (s, 3 H), 2.07 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 124.66, 120.21, 116.52, 114.24, 15.59, 13.44. Mass spectrum, *m/e*, calcd for $C_{13}H_{16}Cl_2Hf$: 422.0096. Found: 422.0109.

Anal. Calcd for $C_{13}H_{16}Cl_2Hf$: C, 37.03; H, 3.82. Found: C, 37.30; H, 3.87.

1,2,4-Trimethylhafnocene Dibromide (2b). Into a 100-mL Schlenk flask was added 1,2,4-trimethylhafnocene dichloride (**2a**) (0.208 g, 0.494 mmol) and 15 mL of methylene chloride. To the stirred solution under nitrogen was added 0.6 mL (0.60 mmol) of a 1.0 M solution of boron tribromide in methylene chloride. The solution was stirred for 1 h, and then the volatiles were removed under reduced pressure. The resultant solid was taken up in 30 mL of methylene chloride, the solution was filtered, and the filtrate was concentrated. Crystallization was induced by addition of hexane to afford 0.164 g (65% yield) of light green needles: mp (sealed tube) 193–194 °C dec; IR (KBr) 3105, 2950, 2920, 1515, 1487, 1445, 1389, 1138, 1131, 1026, 1018, 899, 843, 816 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.36 (s, 5 H), 6.02 (s, 2 H), 2.26 (s, 3 H), 2.19 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 124.74, 119.74, 117.71, 114.46, 16.22, 14.42. Mass spectrum, *m/e*, calcd for $C_{13}H_{16}Br_2Hf$: 509.9085. Found: 509.9062.

Anal. Calcd for $C_{13}H_{16}Br_2Hf$: C, 30.58; H, 3.16. Found: C, 30.90; H, 3.16.

1,2,4-Trimethylhafnocene Diiodide (2c). Into a 50-mL Schlenk flask was placed 1,2,4-trimethylhafnocene dichloride (**2a**) (0.177 g, 0.419 mmol) and 15 mL of methylene chloride. To the stirred solution under nitrogen was added 0.43 mL (0.43 mmol) of a 1.0 M solution of boron triiodide in methylene chloride. The mixture was stirred for 1 h, and then the volatiles were removed under reduced pressure. The resultant yellow solid was sublimed at 120 °C (0.05 mm) to afford 0.124 g (50% yield) of a bright yellow solid: mp (sealed tube) >300 °C dec; IR (KBr) 3110, 2950, 2920, 1516, 1446, 1390, 1138, 1025, 1018, 898, 844, 819 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.43 (s, 5 H), 6.23 (s, 2 H), 2.30 (s, 6 H), 2.23 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 124.24, 119.03, 118.48, 114.02, 16.95, 15.93. Mass spectrum, *m/e*, calcd for $C_{13}H_{16}I_2Hf$: 605.8809. Found: 605.8779.

Anal. Calcd for $C_{13}H_{16}I_2Hf$: C, 25.83; H, 2.67. Found: C, 25.97; H, 2.73.

1,2,3,4,5-Pentamethylhafnocene Dichloride (3a). Into a 250-mL Schlenk tube was placed (η^5-pentamethylcyclopentadienyl)hafnium trichloride (**9**) (8.0 g, 19 mmol), cyclopentadienyllithium (2.16 g, 30 mmol), and 100 mL of toluene. The resultant mixture was refluxed for 3 days. The volatiles were removed under reduced pressure to give an off-white solid. This solid was taken up in 200 mL of methylene chloride and washed with 100 mL of 3 N hydrochloric acid. The methylene chloride layer was separated, dried over anhydrous magnesium sulfate, and filtered, and the methylene chloride was removed under reduced pressure. The resultant off-white solid was recrystallized from methylene chloride/hexane to afford 6.16 g (72% yield) of off-white crystals: mp (sealed tube) 221–222 °C; IR (KBr) 3132, 3090, 2980, 2955, 2928, 1855, 1750, 1656, 1492, 1458, 1396, 1388, 1136, 1081, 1037, 1025, 920, 892, 826 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.14 (s, 5 H), 2.07 (s, 15 H); ^{13}C NMR (CDCl$_3$) δ 122.25, 114.50, 11.96. Mass spectrum, *m/e*, calcd for $C_{15}H_{20}Cl_2Hf$: 450.0408. Found: 450.0380.

Anal. Calcd for $C_{15}H_{20}Cl_2Hf$: C, 40.06; H, 4.48. Found: C, 40.24; H, 4.56.

1,2,3,4,5-Pentamethylhafnocene Dibromide (3b). Into a 50-mL Schlenk flask was placed 1,2,3,4,5-pentamethylhafnocene dichloride (**3a**) (0.706 g, 1.57 mmol) and 20 mL of methylene chloride. To the stirred solution under nitrogen was added 2.0 mL (2.0 mmol) of a 1.0 M solution of boron tribromide in methylene chloride. The solution was stirred for 1 h, and the volatiles were removed under reduced pressure. The resultant solid was taken up in 20 mL of methylene chloride, the solution was filtered, and the filtrate was concentrated. Crystallization was induced by addition of hexane to afford 0.723 g (86% yield) of light green crystals: mp (sealed tube) 252 °C dec; IR (KBr) 3120, 3078, 2965, 2940, 2910, 1850, 1742, 1658, 1485, 1451, 1422, 1382, 1369, 1131, 1075, 1030, 1018, 917, 838, 825 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.23 (s, 5 H), 2.14 (s, 15 H); ^{13}C NMR (CDCl$_3$) δ 122.78, 114.57, 12.78. Mass spectrum, *m/e*, calcd for $C_{15}H_{20}Br_2Hf$: 537.9398. Found: 537.9400.

Anal. Calcd for $C_{15}H_{20}Br_2Hf$: C, 33.45; H, 3.74. Found: C, 33.76; H, 3.87.

1,2,3,4,5-Pentamethylhafnocene Diiodide (3c). Into a 50-mL Schlenk tube was placed 1,2,3,4,5-pentamethylhafnocene dichloride (**3a**) (0.584 g, 1.30 mmol) and 20 mL of methylene chloride. To the stirred solution under nitrogen was added 1.30 mL (1.30 mmol) of a 1.0 M solution of boron triiodide in methylene chloride. The solution was stirred for 1 h, and then the solvent was removed under reduced pressure. The resultant solid was taken up in 25 mL of methylene chloride, the solution was filtered, and the filtrate was concentrated. Crystallization was induced by addition of hexane to afford 0.623 g (76% yield) of bright yellow crystals: mp (sealed tube) >300 °C dec; IR (KBr) 3210, 3120, 3080, 2950, 2910, 1850, 1745, 1658, 1485, 1454, 1424, 1395, 1383, 1196, 1075, 1030, 1019, 919, 827 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.25 (s, 15 H), 2.21 (s, 5 H); ^{13}C NMR (CDCl$_3$) δ 123.22, 114.14, 14.37. Mass spectrum, *m/e*, calcd for $C_{15}H_{20}I_2Hf$: 633.9122. Found: 633.9100.

Anal. Calcd for $C_{15}H_{20}I_2Hf$: C, 28.47; H, 3.18. Found: C, 28.70; H, 3.27.

1,1′,2,2′,4,4′-Hexamethylhafnocene Dichloride (4a). Into a 50-mL Schlenk tube was placed 1,2,4-trimethylcyclopentadienyllithium (**8**) (0.81 g, 7.1 mmol), hafnium tetrachloride (1.00 g, 3.12 mmol), and 25 mL of toluene. The resultant mixture was refluxed for 5 days. The volatiles were removed under reduced pressure to give a tan solid. This solid was taken up in 75 mL of methylene chloride and washed with 75 mL of 3 N hydrochloric acid. The methylene chloride layer was separated, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was concentrated. Crystallization was induced by addition of hexane to afford 0.745 g (52% yield) of long white needles: mp (sealed tube) 156–157 °C; IR (KBr) 3093, 2982, 2955, 2910, 1530, 1482, 1459, 1442, 1420, 1392, 1384, 1135, 1040, 1030, 968, 918, 882, 851, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.88 (s, 4 H), 2.22 (s, 6 H), 2.11 (s, 12 H); ^{13}C NMR (CDCl$_3$) δ 124.34, 119.05, 116.79, 15.29, 13.28. Mass spectrum, *m/e*, calcd for $C_{16}H_{22}Cl_2Hf$: 464.0564. Found: 464.0572.

Anal. Calcd for $C_{16}H_{22}Cl_2Hf$: C, 41.44; H, 4.78. Found: C, 42.01; H, 4.79.

1,1′,2,2′,4,4′-Hexamethylhafnocene Dibromide (4b). Into a 50-mL Schlenk flask was placed 1,1′,2,2′,4,4′-hexamethylhafnocene dichloride (**4a**) (0.188 g, 0.404 mmol) and 15 mL of methylene chloride. To the stirred solution under nitrogen was added 0.60 mL (0.60 mmol) of a 1.0 M solution of boron tribromide in methylene chloride. The mixture was stirred for 1 h, and the volatiles were then removed under reduced pressure. The resultant solid was taken up in 20 mL of methylene chloride, the solution was filtered, and the filtrate was concentrated. Crystallization was promoted by addition of hexane to afford 0.121 g (54% yield) of light green needles: mp (sealed tube) 154–156 °C; IR (KBr) 3110, 3090, 2985, 2956, 2919, 1518, 1487, 1460, 1396, 1386, 1138, 1033, 910, 880, 853 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.92 (s, 4 H), 2.18 (s, 6 H), 2.13 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 124.57, 118.78, 117.77, 15.87, 14.28. Mass spectrum, *m/e*, calcd for $C_{16}H_{22}Br_2Hf$: 551.9554. Found: 551.9567.

Anal. Calcd for $C_{16}H_{22}Br_2Hf$: C, 34.77; H, 4.01. Found: C, 35.18; H, 4.03.

1,1′,2,2′,4,4′-Hexamethylhafnocene Diiodide (4c). Into a 50-mL Schlenk flask was placed 1,1′,2,2′,4,4′-hexamethylhafnocene dichloride (**4a**) (0.147 g, 0.316 mmol) and 15 mL of methylene chloride. To the stirred solution under nitrogen was added 0.35 mL (0.35 mmol) of a 1.0 M solution of boron triiodide in methylene chloride. The mixture was stirred for 1 h, and the volatiles were then removed under reduced pressure. The resultant yellow solid was sublimed at 120 °C (0.05 mm) to afford 0.105 g (51% yield) of a bright yellow solid: mp (sealed tube) 238 °C dec; IR (KBr) 3090, 2975, 2952, 2916, 1513, 1480, 1456, 1387, 1132, 1027, 889, 876, 605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.15 (s, 4 H), 2.23 (s, 12 H), 2.15 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 124.43, 118.38, 118.29, 16.34, 16.08. Mass spectrum, *m/e*, calcd for $C_{16}H_{22}I_2Hf$: 647.9811. Found: 647.9864.

Anal. Calcd for $C_{16}H_{22}I_2Hf$: C, 29.72; H, 3.43. Found: C, 30.14; H, 3.50.

1,1′,2,2′,3,4,4′,5-Octamethylhafnocene Dichloride (5a). Into a 200-mL Schlenk flask was placed (η^5-pentamethylcyclopentadienyl)hafnium trichloride (**9**) (4.70 g, 11.8 mmol), 1,2,4-trimethylcyclopentadienyllithium (**8**) (1.90 g, 17.7 mmol), and 100 mL of toluene. The resultant mixture was refluxed for 2 days. The volatiles were removed under reduced pressure to yield a pale yellow solid. This solid was taken up in 100 mL of methylene chloride and washed with 100 mL of 3 N hydrochloric acid. The methylene chloride layer was separated, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed under reduced pressure. Recrystallization from methylene chloride/hexane afforded 2.82 g (48% yield) of white needles: mp (sealed tube) 176–177 °C; IR (KBr) 3090, 2970, 2945, 2905, 1510, 1491, 1440, 1383, 1131, 1032, 870, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.85 (s, 2 H), 2.06 (s, 15 H), 2.01 (s, 9 H): ^{13}C NMR ($CDCl_3$) δ 124.18, 122.00, 118.45, 116.19, 14.18, 13.01, 12.27. Mass spectrum, *m/e*, calcd for $C_{18}H_{26}Cl_2Hf$: 492.0878. Found: 492.0852.

Anal. Calcd for $C_{18}H_{26}Cl_2Hf$: C, 43.96; H, 5.33. Found: C, 44.09; H, 5.34.

1,1′,2,2′,3,4,4′,5-Octamethylhafnocene Dibromide (5b). Into a 50-mL Schlenk flask was placed 1,1′,2,2′,3,4,4′,5-octamethylhafnocene dichloride (**5a**) (0.217 g, 0.441 mmol) and 15 mL of methylene chloride. To the stirred solution under nitrogen was added 0.60 mL (0.60 mmol) of a 1.0 M solution of boron tribromide in methylene chloride. The mixture was stirred for 1 h, and then the volatiles were removed under reduced pressure. The resultant solid was taken up in 20 mL of methylene chloride, the solution was filtered, and the filtrate was concentrated. Crystallization was induced by addition of hexane to afford 0.160 g (62% yield) of light green needles: mp (sealed tube) 217 °C dec; IR (KBr) 3100, 2983, 2955, 2912, 1514, 1496, 1448, 1388, 1132, 1026, 873 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.98 (s, 2 H), 2.14 (s, 15 H), 2.08 (s, 6 H), 2.04 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 124.29, 122.51, 119.01, 116.95, 14.57, 13.82, 13.06. Mass spectrum, *m/e*, calcd for $C_{18}H_{26}Br_2Hf$: 581.9848. Found: 581.9800.

Anal. Calcd for $C_{18}H_{26}Br_2Hf$: C, 37.23; H, 4.51. Found: C, 37.55; H, 4.58.

1,1′,2,2′,3,4,4′,5-Octamethylhafnocene Diiodide (5c). Into a 50-mL Schlenk tube was placed 1,1′,2,2′,3,4,4′,5-octamethylhafnocene dichloride (**5a**) (0.226 g, 0.460 mmol) and 15 mL of methylene chloride. To the stirred solution under nitrogen was added 0.60 mL (0.60 mmol) of a 1.0 M solution of boron triiodide in methylene chloride. The reaction mixture was stirred for 1 h, and the volatiles were then removed under reduced pressure. The resultant solid was taken up in 25 mL of methylene chloride, the solution was filtered, and the filtrate was concentrated. Crystallization was induced by addition of hexane to afford 0.172 g (55% yield) of golden yellow needles: mp (sealed tube) >300 °C dec; IR (KBr) 2983, 2955, 2905, 1512, 1495, 1450, 1388, 1026, 873 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.20 (s, 2 H), 2.25 (s, 15 H), 2.21 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 124.35, 123.12, 119.42, 117.20, 15.61, 15.24, 14.27. Mass spectrum, *m/e*, calcd for $C_{18}H_{26}I_2Hf$: 675.9596. Found: 675.9576.

Anal. Calcd for $C_{18}H_{26}I_2Hf$: C, 32.04; H, 3.88. Found: C, 32.34; H, 3.96.

1,1′,2,2′,3,3′,4,4′,5,5′-Decamethylhafnocene Dibromide (6b). Into a 50-mL Schlenk flask was placed 1,1′,2,2′,3,3′,4,4′,5,5′-decamethylhafnocene dichloride (**6a**) (0.211 g, 0.406 mmol) and 15 mL of methylene chloride. To the stirred solution under nitrogen was added 0.50 mL (0.50 mmol) of a 1.0 M solution of boron tribromide in methylene chloride. The resultant mixture was stirred for 1 h, and then the volatiles were removed under reduced pressure. The solid was taken up in 25 mL of methylene chloride, the solution was filtered, and the filtrate concentrated. Crystallization was induced by addition of hexane to afford 0.200 g (81% yield) of small light yellow needles: mp (sealed tube) >300 °C dec; IR (KBr) 2985, 2955, 2900, 1493, 1455, 1433, 1385, 1026 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.10 (s); ^{13}C NMR ($CDCl_3$) δ 122.53, 12.84. Mass spectrum, *m/e*, calcd for $C_{20}H_{30}Br_2Hf$: 608.1082. Found: 608.1062.

Anal. Calcd for $C_{20}H_{30}Br_2Hf$: C, 39.46; H, 4.97. Found: C, 40.03; H, 5.05.

X-ray Structural Determinations. The single-crystal X-ray determinations were made by using an Enraf-Nonius CAD4 spectrometer at ambient temperatures with the operational parameters described in Table III.[14]

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation. We thank Professor D. Britton for his assistance in the X-ray structure determinations.

Supplementary Material Available: Tables of positional parameters, general thermal factor expressions, bond distances, bond angles, least-squares planes, and interatomic distances for **1b**–**3b** and **6b** (41 pages); listings of observed and calculated structure factors for **1b**–**3b** and **6b** (32 pages). Ordering information is given on any current masthead page.

---

(14) All calculations were carried out on a PDP 11/34 computer with the Enraf-Nonius SDP programs. This crystallographic computing package is described by: Frentz, B. A. In *Computing in Crystallography*; Schenk, H., Oltof-Hazelkamp, R., Von Konigweld, H., Bassie, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.