

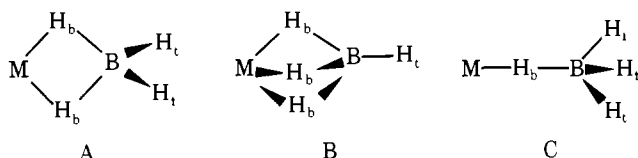
# A Spectroscopic and Neutron Diffraction Investigation of Structure, Bonding, and Molecular Dynamics in Bis(methylcyclopentadienyl)hafnium Bis(tetrahydroborate), $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2^1$

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**Abstract:** The complex  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  can be prepared by the reaction of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{HfCl}_2$  with  $\text{LiBH}_4$  in benzene. The bonding, molecular dynamics, and structure of this compound have been studied by infrared and Raman vibrational spectroscopy, by dynamic nuclear magnetic resonance spectroscopy, and by single-crystal neutron diffraction. Vibrational spectra reveal the perturbation of the boron-containing ligand from a free  $\text{BH}_4^-$  ion to be less in this complex than in most covalent tetrahydroborate transition metal complexes. Exchange of bridge and terminal  $\text{BH}_4^-$  hydrogen atoms is rapid on the 90-MHz  $^1\text{H}$  NMR time scale down to  $-155^\circ\text{C}$ ; thus,  $\Delta G^\ddagger$  for the interchange process is less than ca. 4.9 kcal/mol. The compound crystallizes from toluene/pentane in the monoclinic space group  $C2/c$  with four molecules in a unit cell of dimensions  $a = 14.566$  (3),  $b = 6.839$  (1),  $c = 13.959$  (3) Å, and  $\beta = 102.31$  (2) $^\circ$ . Full-matrix least-squares refinement gave a final value of  $R(F_o^2) = 0.107$  for 1022 reflections. The molecular structure consists of monomeric  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  units having  $C_2$  symmetry and bidentate tetrahydroborate ligands. The ring centroid-Hf-ring centroid angle is  $128.5$  (3) $^\circ$ . The average Hf-C(ring) bond distance is  $2.491$  (9) Å. The coordination of each tetrahydroborate group is markedly unsymmetrical with crystallographically independent Hf-H(bridge) distances of  $2.069$  (7) and  $2.120$  (8) Å. The lengths of the two B-H(bridge) bonds mirror, inversely, the Hf-H distances:  $1.255$  (9) and  $1.208$  (13) Å. The B-H(terminal) distances are  $1.186$  (16) and  $1.198$  (15) Å, and the Hf-B distance is  $2.553$  (6) Å. Important bond angles are B-Hf-B =  $101.4$  (3) $^\circ$ , H(bridge)-B-H(bridge) =  $108.4$  (6) $^\circ$ , and H(terminal)-B-H(terminal) =  $115.4$  (10) $^\circ$ . The anisotropy of the hydrogen atom thermal parameters within the tetrahydroborate groups may reflect motion along the bridge-terminal hydrogen interchange reaction coordinate. The nature of the  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}$ -tetrahydroborate interaction as observed in the vibrational spectra and molecular structure can be understood in terms of those bonding factors which govern ligand-to-metal charge donation.

The transition metal complexes of the tetrahydroborate ligand,  $\text{BH}_4^-$ , exhibit a number of unusual and interesting properties. These include coordination through metal-hydrogen-boron multicenter bonds (A, B, or C), a very low



barrier to intramolecular bridge-terminal ( $\text{H}_b\text{-H}_t$ ) hydrogen interchange, covalent properties reminiscent of organometallic compounds, and, in some cases, catalytic activity.<sup>3</sup> Though considerable progress has been achieved in elaborating the variety of known metal tetrahydroborates and in explaining their chemical and structural/dynamical characteristics, areas of marked deficiency still exist in our understanding. On a general level, there is a paucity of accurate structural data which would allow precise correlation of spectral and metrical parameters with bonding models and chemical reactivity. In several specific instances, compounds are known which do not conform well to existing norms for spectroscopic properties or molecule stoichiometry, and which are not well characterized structurally.

The compounds  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2^{4a,b}$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}(\text{BH}_4)_2^{4c}$  were among the earliest reported organometallic tetrahydroborates. On the basis of infrared and Raman spectroscopic studies, it was deduced<sup>5</sup> that these two complexes (which exhibit essentially identical spectra) possess bidentate (A) coordination geometries, but it was also noted<sup>5</sup> that the vibrational spectra were unlike those of other bidentate transition metal tetrahydroborates.<sup>3a</sup> In particular, the normal modes involving B-H<sub>b</sub> stretching are anomalously high in energy and those involving significant M-H<sub>b</sub> stretching are anomalously low in energy. A qualitative electron counting

scheme assuming an 18-electron valence system suggested that in  $(\text{C}_4\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$  and  $(\text{C}_5\text{H}_5)\text{Hf}(\text{BH}_4)_2$  the bidentate  $\text{BH}_4^-$  ligands could not donate as much electron density as in other transition metal tetrahydroborates (where formal four-electron donation predominates<sup>3a</sup>) and that, to first order, the anomalous vibrational spectra thus reflect a smaller than usual perturbation of the ligand from a free  $\text{BH}_4^-$  ion.<sup>5</sup> Subsequent extended Hückel molecular orbital studies by Lauher and Hoffmann examined the metal-ligand bonding possibilities in  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$ , for various conceivable  $\text{M}(\text{BH}_4)_2$  configurations, and it was concluded that all choices of structure possessed serious defects either in terms of orbital overlap, nonbonded repulsions, or in having to invoke an at that time unprecedented<sup>38</sup> monodentate ligation geometry. More detailed structural data for these complexes were clearly needed. In this paper we report the synthesis and precise solid state structural characterization, by single crystal neutron diffraction, of the compound  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ . We also present a discussion of the vibrational and variable temperature solution nuclear magnetic resonance spectra. What emerges from this work is a considerably more accurate picture of structure, structural dynamics, and bonding in this particular compound and in related transition metal tetrahydroborate complexes.

## Experimental Section

The synthesis and handling of all compounds were carried out under an atmosphere of prepurified nitrogen or in vacuo. Schlenk or glove box techniques were employed for the manipulation of all samples. Solvents for reactions or crystallizations were distilled under nitrogen from sodium/potassium alloy-benzophenone immediately prior to use. Melting points were determined in sealed, nitrogen-filled capillaries and are uncorrected. Elemental analyses were performed by Miss H. Beck, Northwestern Analytical Services Laboratory, or Schwartzkopf Microanalytical Laboratory.

**Bis(methylcyclopentadienyl)hafnium(IV) Dichloride,  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{HfCl}_2$ .** To 11.57 g (40.81 mmol) of  $\text{Ti}(\text{CH}_3\text{C}_5\text{H}_4)_7$  in 250 mL of tol-

uene was added 5.83 g (18.2 mmol) of  $\text{HfCl}_4$  (Alfa, vacuum sublimed). The flask was covered with aluminum foil to prevent photo-decomposition of the resulting  $\text{TiCl}_4$ , and the mixture was stirred at reflux for 20 h. After this time, the white reaction slurry was cooled to room temperature and was then suction filtered under nitrogen. The toluene was next removed from the filtrate under vacuum and the crude, white crystalline product was washed twice with 5-mL portions of pentane and vacuum dried. The product was recrystallized several (three to four) times from toluene solution at  $-30^\circ\text{C}$  to yield 6.1 g (82%) of bis(methylcyclopentadienyl)hafnium dichloride as a white, moisture-sensitive, crystalline solid, mp  $169.5\text{--}170.0^\circ\text{C}$ .

Anal. Calcd for  $\text{C}_{12}\text{H}_{14}\text{HfCl}_2$ : C, 35.36; H, 3.46. Found: C, 35.26, H, 3.52.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.13 (multiplet, 8 H), 2.33 (singlet, 6 H).

**Bis(methylcyclopentadienyl)hafnium(IV) Bistetrahydroborate**,  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ . This is a modification of the procedure of James and Smith<sup>8</sup> for the unmethylated analogue. To 0.70 g (32 mmol) of  $\text{LiBH}_4$  suspended in 100 mL of benzene was added 2.85 g (6.98 mmol) of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{HfCl}_2$ . The mixture was stirred at room temperature for 15 h, at which time it was suction filtered under nitrogen. The colorless filtrate was then concentrated in vacuo to ca. 12 mL. This solution was syringed into 150 mL of pentane maintained at  $-40^\circ\text{C}$ . Next, the mixture was filtered while cold and the white, crystalline precipitate was collected, washed with 5 mL of pentane, and dried under high vacuum. The product can be further purified by recrystallization from toluene/pentane mixtures at  $-30^\circ\text{C}$ . By this procedure, bis(methylcyclopentadienyl)hafnium bistetrahydroborate is obtained in 70–80% yield as white, highly moisture-sensitive crystals, mp  $112.5\text{--}113.5^\circ\text{C}$  dec.

Anal. Calcd for  $\text{C}_{12}\text{H}_{22}\text{HfB}_2$ : C, 39.33; H, 6.05; B, 5.90. Found: C, 39.45; H, 6.31; B, 5.79.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  5.56 (multiplet, 8 H), 2.08 (singlet, 6 H), 1.53 (8 H, quartet,  $J_{\text{B-H}} = 84\text{ Hz}$ ).

The above procedure can also be employed for the synthesis of the zirconium analogue, which will be discussed elsewhere.<sup>9</sup>

**Spectroscopic Measurements.** Infrared spectra were recorded on a Perkin-Elmer 267 spectrophotometer and were calibrated with polystyrene film. Nujol mulls were prepared in a nitrogen-filled glove box with dry, degassed Nujol. Samples were monitored for possible decomposition by observing whether changes occurred over the course of several scans. Mulls samples were also deliberately exposed to air to ascertain the effect on samples. In the case of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ , exposure to air produced a marked decay of the B–H stretching absorptions and the appearance of strong bands at 805 and  $3300\text{ cm}^{-1}$  (broad), assignable, respectively, to the antisymmetric M–O–M stretch of a  $\mu$ -oxo dimer,<sup>10</sup> and to water or hydroxide.

Raman spectra were recorded with  $\text{Kr}^+$  (6471 Å) or  $\text{Ar}^+$  (5145 Å) excitation employing a Spex Model 1401 monochromator and photon counting detection. Considerably less fluorescence was encountered with the  $\text{Kr}^+$  frequency. The solid samples were studied in 5- or 12-mm spinning (1800 rpm) Pyrex sample tubes. Several scans were taken to identify lines which might grow in intensity due to decomposition (none were observed).

Nuclear magnetic resonance spectra (CW  $^1\text{H}$ ) were obtained with Perkin-Elmer R20-B (60 MHz) or Bruker HFX-90 (90 MHz) instruments. Heteronuclear  $^{11}\text{B}$  decoupling was accomplished with the equipment described previously.<sup>11</sup> Low-temperature studies were performed in Freon solvents ( $\text{CF}_2\text{Cl}_2$ ,  $\text{CFHCl}_2$ ) which had been trap-to-trap distilled and freeze-thaw degassed. Samples of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  in these solvents were sealed off in NMR tubes on a vacuum line and were stored frozen until low-temperature experiments could be conducted. Spectrometer temperatures were calibrated by thermocouple, employing a sample tube of acetone placed directly in the probe.

**Crystallographic Studies.** Crystals of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ , suitable for neutron diffraction studies, were grown by very slow cooling of toluene solutions layered with pentane. The crystal chosen for structural studies, weighing 44.3 mg, was sealed under nitrogen in a lead glass capillary to prevent decomposition by air and moisture. The approximate dimensions were  $1.23 \times 5.13 \times 4.72\text{ mm}$ .

Preliminary x-ray diffraction studies indicated that this compound has monoclinic symmetry and a C-centered space group. The cell constants were established for the present study with a Syntex P2<sub>1</sub> x-ray diffractometer, by centering 15 reflections in the  $2\theta$  range of  $20\text{--}25^\circ$  and carrying out a least-squares fit of the angles  $2\theta$ ,  $\chi$ , and  $\varphi$  of these reflections. Using an x-ray wavelength of  $0.71069\text{ Å}$ , the results were  $a = 14.566(3)\text{ Å}$ ,  $b = 6.839(1)\text{ Å}$ ,  $c = 13.959(3)\text{ Å}$ , and

$\beta = 102.31(2)^\circ$ . The calculated crystal density for four formula units per unit cell ( $V = 1358.6\text{ Å}^3$ ) is  $1.78\text{ g/cm}^3$ . Owing to the high reactivity of this compound, the density could not be measured experimentally.

An Electronics and Alloys four-circle diffractometer located at the CP-5 research reactor of Argonne National Laboratory was used to collect neutron diffraction data ( $\lambda = 1.142(1)\text{ Å}$ ). This fully automated diffractometer is operated under the remote control of the Chemistry Division Sigma V computer. The monochromatic beam results from use of a Be single crystal monochromator, with monochromator angle  $\theta_m = 30^\circ$ , yielding a neutron flux of  $\sim 2.9 \times 10^6\text{ N cm}^{-2}\text{ s}^{-1}$ .

A  $\theta$ - $2\theta$  step-scan technique was used to collect data (step size equals  $0.1^\circ$  in  $2\theta$ ). At each extremity of the scan, a background was established with the crystal and counter being stationary. A total of 1218 reflections were collected, of which 1122 were unique. Of these 1122 reflections, 100 were of the type  $h0l$  and were systematically absent when  $l$  was odd, which establishes the space group as either  $C2/c$  or  $Cc$ . Of the 1122 reflections in the data set, 695 were observed to have intensities greater than one times their standard deviation. This represents a complete data set out to a maximum  $2\theta = 80^\circ$  which is a minimum  $d$  spacing of  $0.888\text{ Å}^{-1}$ . Beyond  $2\theta = 80^\circ$ , the reflections were too weak for accurate measurement. Instrument and crystal stability were monitored by remeasuring two standard reflections every 80 reflections in order to establish the reliability of the data; their combined intensities did not vary more than 4% during data collection.

Structure factors were derived by applying Lorentz and absorption corrections ( $\mu_{\text{calcd}} = 5.35\text{ cm}^{-1}$ ) and the magnitude of the latter correction ranged from 1.92 to 7.69. Using the absorption corrected integrated intensities, the  $F_o^2$  were obtained by application of the equation  $F_o^2 = (wI \sin 2\theta)/(I_0\lambda^3N^2V)$ , where  $I_0$  is the incident intensity,  $\lambda$  is the wavelength,  $w$  is the angular velocity of rotation of the crystal,  $N$  is the number of unit cells per unit volume,  $V$  is the specimen volume, and  $\theta$  is the Bragg angle. A cylindrical NaCl crystal, for which precise absorption and secondary extinction corrections had been made, was used to obtain  $I_0$  and thereby place the  $F_o^2$  on an approximately "absolute" scale. The variances of  $F_o^2$  were calculated from  $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.05F_o^2)^2$ , where  $\sigma_c^2(F_o^2)$  is determined from the counting statistics and 0.05 is an added factor to account for systematic (nonrandom) error.

Initially the structural solution was attempted using the centrosymmetric space group  $C2/c$ . The structure was solved using MULTAN<sup>12a</sup> from which the positions of all nonhydrogen atoms were located. A full-matrix least-square refinement<sup>12b</sup> of the Hf, B, and C positional parameters and isotopic thermal parameters was carried out. A difference Fourier map was then calculated and the hydrogen atoms were located. All atom positional parameters were then refined to convergence (four cycles) and the following discrepancy indices were obtained.

$$R_{F_o} = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.29$$

$$R(F_o^2) = \frac{\sum |F_o^2 - F_c^2|}{\sum F_o^2} = 0.31$$

$$R_w(F_o^2) = \left[ \frac{\sum w_i |F_o^2 - F_c^2|}{\sum w_i F_o^4} \right]^{1/2} = 0.37$$

using all data. Then an additional four cycles of least-squares refinement, including anisotropic thermal parameters and an isotropic extinction parameter, yielded  $R(F_o) = 0.150$ ,  $R(F_o^2) = 0.107$ , and  $R_w(F_o^2) = 0.124$  using all data. Fourier and difference density maps were again calculated and the largest positive peak on the latter Fourier map was only 3% of the largest peak on the Fourier map. These results appeared to support our initial choice of space group  $C2/c$  and therefore no attempt was made to refine the data in the space group  $Cc$ . The final refinement with anisotropic thermal parameters and isotropic extinction ( $g = 0.002(8) \times 10^4$ ) converged yielding the agreement factors in Table I. Intensity statistics relevant to the choice of the centrosymmetric space group are given in Table II.

The standard deviation of an observation of unit weight,

$$\sigma_1 = \left[ \frac{w_i |F_o^2 - F_c^2|^2}{(n - p)} \right]^{1/2}$$

**Table I.** Final Discrepancy Indices

Data selection	No. of reflections	$R(F_o)$	$R(F_o^2)$	$R_w(F_o^2)$	$\sigma_1$
All reflections	1022	0.150	0.107	0.124	1.15
$F_o^2 > 1.0\sigma(F_o^2)$	695	0.090	0.091	0.117	1.37

<sup>a</sup> See Experimental Section for explanation of  $R(F_o)$ ,  $R(F_o^2)$ ,  $R_w(F_o^2)$ , and  $\sigma_1$ .

**Table II.** Intensity Statistics for  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ 

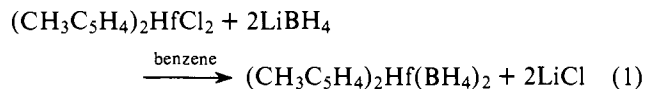
Experimental	Theoretical	
	Centrosymmetric	Noncentrosymmetric
$E^2$	1.000	1.000
MOD ( $E^2 - 1$ )	0.9884	0.9680
MOD ( $E$ )	0.7671	0.7980

where  $n$  is the number of observations and  $p$  the number of parameters varied (169) in the least-squares refinement, was 1.15 for all the data and the ratio of observations to parameters was 6.1:1.

The final positional and thermal parameters are listed in Table III, and root-mean-square amplitudes of vibration in Table IV. The final values of  $10|F_o|$  and  $10|F_c|$  will appear in the microfilm edition.<sup>12c</sup> For the least-squares refinement, the coherent neutron scattering amplitudes used for Hf, C, B, and H were respectively 0.78, 0.663, 0.54 + 0.021*i*, and -0.372, all in units of  $10^{-12}$  cm.

## Results

**Synthesis and Spectral Properties.** The new compound  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  can be prepared in high yield via the route shown in the equation



Methyl substitution of the cyclopentadienyl ligands was chosen to render the complex more readily crystallizable and to minimize ring libration and disorder, which is a common problem in structure determinations on  $\eta^5\text{-C}_5\text{H}_5$  metal complexes.<sup>13</sup> It was also of interest to ascertain if the  $\text{BH}_4^-$ -ring hydrogen interchange process previously observed in the  $(\text{C}_5\text{H}_4)_2\text{M}(\text{BH}_4)_2$  complexes<sup>14</sup> also occurred in this system and whether it included the methyl hydrogens. This work will be discussed separately.<sup>9</sup>

Infrared spectra of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  and  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{HfCl}_2$  are presented in Figure 1. These data and

the corresponding Raman data are set out in Table V. Comparison of the spectra of the bistetrahydroborate and dichloride complexes allows identification of the transitions arising from the coordinated  $\text{BH}_4^-$  moieties. The tetrahydroborate band pattern thus obtained is essentially identical with that already reported for  $(\text{C}_4\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$  and  $(\text{C}_4\text{H}_5)_2\text{Hf}(\text{BH}_4)_2$ .<sup>5,15a</sup> The spectral features are generally in good accord with a bidentate (A) structure<sup>3a,5</sup> having approximately  $C_{2v}$  local symmetry (the actual symmetry will be seen to be slightly lower but does not affect qualitative arguments). Invoking the reasonable simplification that kinematic coupling between oscillators on different  $\text{BH}_4^-$  groups is small, the bands at 2398 and 2444  $\text{cm}^{-1}$  are assignable<sup>3a</sup> under  $C_{2v}$  symmetry to the infrared and Raman-active symmetrically and antisymmetrically coupled B-H<sub>t</sub> stretching modes ( $A_1, B_1$ ).<sup>3,15b,c</sup> The bands at 2160 (infrared) and 2169, 2210  $\text{cm}^{-1}$  (Raman) are logically assigned<sup>3a</sup> to the symmetrically and antisymmetrically coupled B-H<sub>b</sub> stretching modes ( $A_1, B_2$ ).<sup>3,15b,c</sup> The energy of these latter transitions is surprisingly high (the normal range is 1650–1950  $\text{cm}^{-1}$ <sup>3a</sup>). Conversely, the energy of the  $A_1$  "bridge stretching" mode (which probably has considerable  $\nu_{\text{M-H}_b}$  character<sup>3a</sup>) at 1340  $\text{cm}^{-1}$  in the infrared (broad) is somewhat low (the normal range extends as high as 1500  $\text{cm}^{-1}$ <sup>3a</sup>). The infrared-active 1120- $\text{cm}^{-1}$  transition is in the usual region for the  $B_2$   $\text{BH}_2$  deformation mode<sup>3a</sup>. Clearly the methylcyclopentadienyl complex exhibits the same vibrational spectroscopic anomalies as the unmethylated derivatives; these are localized primarily in the  $\text{Hf}(\text{H}_b)_2\text{B}$  portion of the molecule.

The <sup>11</sup>B-decoupled proton nuclear magnetic resonance spectrum of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  exhibits a single  $\text{BH}_4^-$  resonance at  $\delta$  1.53. This is evidence of rapid bridge-terminal ( $\text{H}_b\text{-H}_t$ ) hydrogen atom interchange. In the solvent system 1/1  $\text{CH}_2\text{Cl}_2/\text{CF}_2\text{Cl}_2$ , it was possible to record 90 MHz solution NMR spectra down to -155 °C. Though some broadening of the tetrahydroborate resonance relative to the methyl resonance does occur below ca. -140 °C, it is evident that the hydrogen interchange process is still rapid on the 90 MHz NMR time scale at these temperatures.

**Crystal Structure of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ .** The compound  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  crystallizes in the space group  $C2/c$  with four monomeric molecules in the unit cell. A stereoscopic packing diagram is shown in Figure 2. Final atomic positional and thermal parameters are collected in Table III. There are no unusually short intermolecular contacts.

A perspective view of a single  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$

**Table III.** Atomic Coordinates in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  ( $\times 10^4$ ) and Anisotropic Thermal Parameters ( $\text{\AA}^2 \times 10^4$ ) Corresponding to the Expression  $\exp[8\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hkU_{12}hka^*b^* + \dots)]$ 

	X	Y	Z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Hf	0	5025(5)	7500	33(1)	149(8)	43(2)	0	11(1)	0
Cl	1223(2)	7491(7)	8134(5)	36(2)	252(11)	127(5)	-19(4)	16(2)	-8(6)
C2	932(2)	7799(8)	7118(5)	40(2)	321(13)	151(5)	-9(4)	22(3)	89(7)
C3	1211(3)	6168(8)	6637(4)	51(2)	620(19)	55(3)	-16(5)	15(2)	68(6)
C4	1688(2)	4887(7)	7368(3)	47(2)	396(12)	72(3)	35(4)	21(2)	-20(6)
C5	1717(2)	5738(6)	8272(3)	34(1)	355(11)	60(2)	2(3)	7(2)	12(4)
Cm	2298(5)	4992(15)	9238(5)	65(3)	701(29)	72(4)	-20(9)	-8(3)	30(11)
B	-187(5)	2661(8)	6056(4)	115(4)	202(12)	61(4)	27(7)	4(3)	-28(6)
H1	1133(7)	8450(16)	8674(10)	74(5)	432(32)	205(14)	-64(10)	21(7)	-127(17)
H2	568(6)	9000(16)	6759(12)	78(5)	462(31)	334(20)	-4(11)	34(8)	263(22)
H3	1094(6)	5980(24)	5863(8)	92(6)	1351(73)	72(7)	-53(18)	34(5)	47(20)
H4	2001(6)	3536(17)	7258(9)	80(5)	628(39)	167(10)	102(12)	42(6)	-67(17)
H <sub>b</sub> (1)	-373(5)	4456(11)	6012(5)	87(4)	316(23)	69(5)	30(7)	11(4)	-8(8)
H <sub>b</sub> (2)	225(8)	2281(11)	6882(7)	193(9)	270(20)	71(7)	71(11)	15(7)	-6(10)
H <sub>t</sub> (1)	368(8)	2421(19)	5557(8)	162(9)	613(41)	111(8)	70(16)	44(8)	-64(15)
H <sub>t</sub> (2)	-901(9)	1748(15)	5822(10)	183(11)	371(27)	166(12)	-66(15)	-37(9)	-50(15)
H5	2952(9)	5499(27)	9342(9)	94(7)	1148(79)	110(9)	-23(21)	-16(7)	51(22)
H6	2018(9)	5462(34)	9803(9)	122(8)	1456(107)	68(7)	64(25)	5(7)	72(25)
H7	2350(13)	3615(29)	9274(14)	147(12)	794(66)	135(14)	118(26)	-38(10)	101(28)

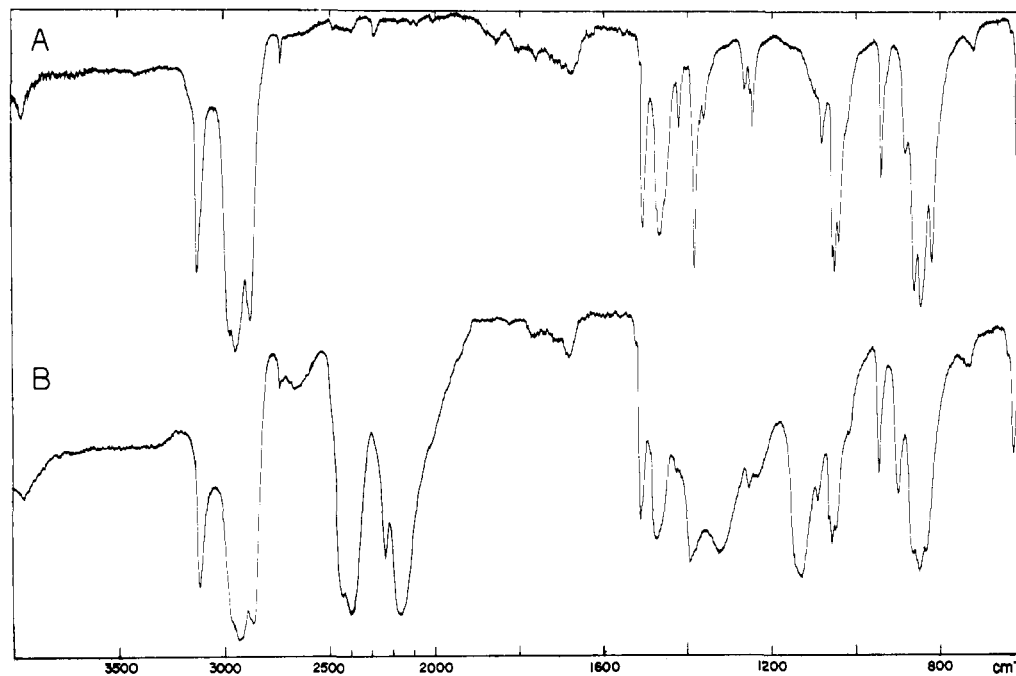


Figure 1. Infrared spectra of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{HfCl}_2$  (A) and  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  (B) as Nujol mulls.

Table IV. Root-Mean-Square Amplitudes of Vibration along Principal Ellipsoid Axes (Å)

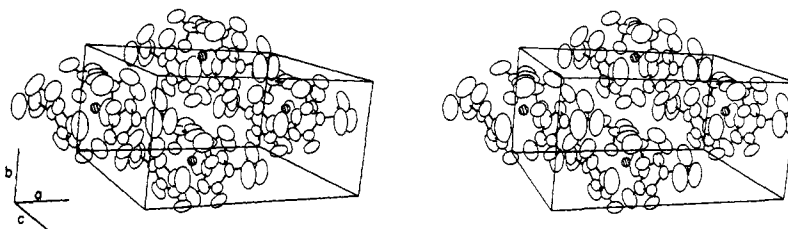
Atom	Minimum	Intermediate	Maximum
Hf	0.180 (4)	0.188 (5)	0.203 (5)
C1	0.181 (5)	0.251 (6)	0.347 (6)
C2	0.187 (5)	0.243 (6)	0.405 (6)
C3	0.191 (6)	0.234 (5)	0.398 (6)
C4	0.189 (6)	0.263 (5)	0.320 (5)
C5	0.187 (4)	0.238 (5)	0.292 (5)
Cm	0.220 (8)	0.301 (7)	0.413 (9)
B	0.194 (8)	0.250 (8)	0.360 (7)
H1	0.221 (12)	0.319 (13)	0.473 (14)
H2	0.216 (12)	0.286 (10)	0.617 (18)
H3	0.225 (13)	0.313 (10)	0.571 (16)
H4	0.197 (12)	0.382 (12)	0.444 (13)
H <sub>b</sub> (1)	0.252 (9)	0.258 (9)	0.319 (8)
H <sub>b</sub> (2)	0.234 (10)	0.260 (13)	0.462 (12)
H <sub>i</sub> (1)	0.265 (13)	0.380 (13)	0.442 (13)
H <sub>i</sub> (2)	0.248 (13)	0.368 (13)	0.517 (15)
H5	0.263 (12)	0.375 (14)	0.528 (18)
H6	0.240 (13)	0.363 (13)	0.593 (22)
H7	0.223 (17)	0.459 (22)	0.486 (21)

Table V. Infrared and Raman Spectral Data for  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{HfCl}_2$  and  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ <sup>a</sup>

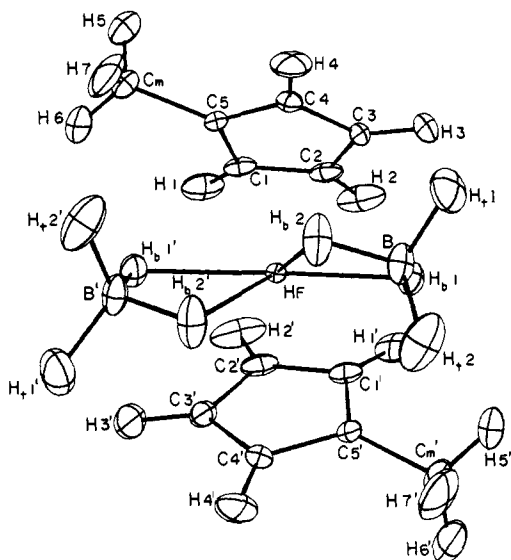
$(\text{CH}_3\text{C}_5\text{H}_4)_2\text{HfCl}_2$		$(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$	
Infrared <sup>b</sup>	Raman <sup>c</sup>	Infrared	Raman
3120 mw	3120 s	3120 mw	3118 m
	3100 m		3097 mw
	2960 w		2960 w
	2935 ms		2937 m
	2950 vw		2900 w
2739 vw	2860 vw	2740 vw	2860 vw
		2444 s	2440 m
		2398 s	2398 ms
		2235 w	2210 m
		2160 s	2169 m
1505 w	1502 w	1501 w	1500 w
	1455 w		1451 vw
	1370 w		1365 w
		1340 ms,br	
1255 vw	1255 m	1264 vw	1255 m
1245 w	1245 mw	1232 w,br,sh	1230 w,sh
		1120 s	1120 m
1080 w	1078 m	1081 w	1078 ms
1054 mw	1052 ms	1056 w	1052 ms
1049 m	1045 w	1038 mw	1045 w
1038 mw		1030 mw	
940 w	940 m	944 w	940 m
		930 w	
860 m	860 w	879 mw	860 w
841 mw		841 s	
818 m	820 w		
		722 mw	
620 w	640 m	621 w	640 m
	620 w		625 vw
	365 m		364 w
	345 w		345 w,sh
	320 vs		320 vs
	295 w		296 w,br
	258 m		260 w
	190 m		190 vs,br
	145 s		
	130 s		125 mw

molecule showing the atom labeling scheme is presented in Figure 3. A stereoscopic view from a different direction is shown in Figure 4. The point group of the molecule is  $C_2$  with the two *bidentate* tetrahydroborate ligands as well as the two pentahapto(methylcyclopentadienyl) rings related by the twofold axis. Selected bond distances and angles are compiled in Table VI. The coordination geometry about the hafnium ion is the distorted tetrahedral, "tilted sandwich" configuration common for  $(\text{C}_5\text{H}_5)_2\text{ML}_n$  compounds. It can be most closely compared to the structures of  $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$ ,<sup>10a</sup>  $[(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)]_2\text{O}$ ,<sup>10a</sup>  $(\text{C}_5\text{H}_5)_2\text{HfC}_4(\text{C}_6\text{H}_5)_4$ ,<sup>16</sup>  $(\text{CH}_2)_3\text{-(C}_5\text{H}_4)_2\text{HfCl}_2$ ,<sup>17</sup> and  $(\text{C}_5\text{H}_5)_4\text{Hf}$ .<sup>18</sup> The ring centroid-Hf-ring centroid angle in the present structure is  $128.5(3)^\circ$ , which compares favorably with corresponding angles in the above first four structures of  $132.1$ ,<sup>10a</sup>  $128.5$ ,<sup>10a</sup>  $134$ ,<sup>16</sup> and  $129.5$ ,<sup>17</sup> respectively. Typical values for other  $d^0(\text{C}_5\text{H}_5)_2\text{ML}_2$  compounds are in the range  $130\text{--}135^\circ$ .<sup>19</sup> The Hf-C(ring) distances in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  range from  $2.456(5)$  to  $2.550(3)$  Å with an average value of  $2.491(9)$  Å. The longest

<sup>a</sup> In  $\text{cm}^{-1}$ , s = strong, m = medium, w = weak, br = broad, sh = shoulder, v = very. Italicized data are assigned to transitions involving the tetrahydroborate ligand. <sup>b</sup> Nujol mull. <sup>c</sup> Polycrystalline sample.



**Figure 2.** Stereoscopic view of the packing of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  in the unit cell. For clarity, only two molecules within the cell are shown and Hf atoms are shaded.



**Figure 3.** Perspective view of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  showing the atom numbering scheme. The 50% probability vibrational ellipsoids are shown.

distance is for C5 (and C5'), which bear the methyl groups. Comparison of these data with the results on  $\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$  and  $[(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2]\text{O}$  is most meaningful since these appear to be the most accurately determined of the prior bis-cyclopentadienylhafnium(IV) structures. For the former complex Hf–C(ring) values range from 2.474 (9) to 2.539 (9) Å with an average of 2.505 (7) Å,<sup>10a</sup> while for the latter, Hf–C(ring) is between 2.487 (13) and 2.531 (13) Å with an average value of 2.513 (5) Å.<sup>10a</sup> Similarly, the Hf–ring centroid distance in the present determination is 2.188 (4) Å, while for  $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$  it is 2.210 Å<sup>10a</sup> and for  $[(\text{C}_5\text{H}_4)_2\text{Hf}(\text{CH}_3)_2]\text{O}$  it is 2.225 Å.<sup>10a</sup> The ring carbon–carbon distances in the  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  structure range from 1.382 (5) to 1.411 (6) Å (1.399 (4) Å average) with the two distances to the methyl-substituted ring carbon atom being slightly longer. Average carbon–carbon distances for  $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$  and  $[(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2]\text{O}$  are 1.383 (11)<sup>10a</sup> and 1.380 (16) Å,<sup>10a</sup> respectively. The cyclopentadienyl rings in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  are essentially planar with the maximum deviation of a carbon atom from the unit-weighted least-squares mean plane (Table VII) being 0.023 (4) Å. The ring hydrogen atoms are displaced from this plane by no greater than 0.037 (10) Å, while the methyl carbon lies 0.226 (8) Å out of the plane in the direction away from the hafnium atom. This value for the methyl out-of-plane distance can be compared to 0.06 Å in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$  and 0.08 Å in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{VCl}_2$ .<sup>19a</sup> In each of these two structures, the ring methyl groups are displaced only slightly (and in opposite directions) from the ring centroid–metal–ring centroid plane, i.e., 0.29 (Ti) and 0.26 Å (V).<sup>19a</sup> For  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ , this distance is considerably larger, 2.36 (1) Å (see Figure 4), which appears to reflect minimization of nonbonded interactions with the tetrahydroborate ligands.

The coordination geometry associated with the  $\text{BH}_4^-$  groups is by far the most interesting aspect of the present structure. These ligands are bound in a bidentate fashion with the outer bridging hydrogen atoms, i.e.,  $\text{H}_{b1}$  and  $\text{H}_{b1}'$ , lying in the plane which bisects the ring centroid–Hf–ring centroid angle. The  $\text{H}_{b1}\text{-Hf-H}_{b1}'$  angle is quite large—158.3 (4)°. The inner bridging hydrogen atoms,  $\text{H}_{b2}$  and  $\text{H}_{b2}'$ , are displaced +0.55 (1) and –0.55 (1) Å from the  $\text{H}_{b1}\text{-Hf-H}_{b1}'$  plane. The dihedral angle between the planes  $\text{H}_{b1}\text{-Hf-H}_{b2}$  and  $\text{H}_{b1}'\text{-Hf-H}_{b2}'$  is 35.5 (7)°. A number of factors probably contribute to the observed twisting of the tetrahydroborate groups from a geometry in which all four bridging hydrogen atoms are coplanar. From structural considerations alone, this twisting appears to reflect steric repulsion between  $\text{H}_{b2}$  and  $\text{H}_{b2}'$  (the  $\text{H}_{b2}\text{-H}_{b2}'$  distance found is a rather short 1.97 (2) Å<sup>20</sup>) and the energetically unfavorable interactions which would occur with the cyclopentadienyl rings if the tetrahydroborate groups were spread further apart rather than twisting them. The B–Hf–B' angle in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  is 101.4 (3)°. Owing to the multidentate nature of the  $\text{BH}_4^-$  ligands, it is difficult to meaningfully compare the degree of ligand “spread” in the present structure with that in other  $(\text{C}_4\text{H}_5)_2\text{HfL}_2$  derivatives. As a point of reference, the angle  $(\text{CH}_3)\text{-Hf-(CH}_3)$  in  $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$ <sup>10a</sup> is 98.4 (3)° and the angle  $(\text{CH}_3)\text{-Hf-O}$  in  $[(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2]\text{O}$ <sup>10a</sup> is 96.9 (5)°.

The coordination of the tetrahydroborate ligands to the hafnium in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  (Figure 5) is significantly unsymmetrical, with  $\text{Hf-H}_{b1}(\text{H}_{b1}') = 2.069$  (7) Å and  $\text{Hf-H}_{b2}(\text{H}_{b2}') = 2.120$  (8) Å; this represents a difference in Hf– $\text{H}_b$  distances of ca. 5 standard deviations. The longer distances are to the “inner” ( $\text{H}_{b2}$ ,  $\text{H}_{b2}'$ ) hydrogen atoms, which are twisted away from the  $\text{H}_{b1}\text{-Hf-H}_{b1}'$  plane as already mentioned. The shorter Hf– $\text{H}_b$  distance compares well with a value of 2.06 (2) Å found in the neutron diffraction study of  $\text{Hf}(\text{BH}_4)_4$ ,<sup>21</sup> which possesses tridentate  $\text{BH}_4^-$  coordination. The Hf–B contact of 2.553 (6) Å in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  is longer, as expected from the different  $\text{BH}_4^-$  ligation geometry, than the Hf–B distance of 2.25 (3) Å in  $\text{Hf}(\text{BH}_4)_4$ .<sup>21</sup>

Within the tetrahydroborate ligand it appears that the B– $\text{H}_b$  distances mirror, inversely, the Hf– $\text{H}_b$  dimensions. This relationship is illustrated in Figure 5. Thus,  $\text{B-H}_{b1}(\text{H}_{b1}') = 1.255$  (9) Å and  $\text{B-H}_{b2}(\text{H}_{b2}') = 1.208$  (13) Å, a difference which represents ca. 3 standard deviations and is in all likelihood significant. The above distances are roughly comparable to B– $\text{H}_b$  distances found for bidentate  $\text{BH}_4^-$  groups in  $\text{U}(\text{BH}_4)_4$  (1.25 (4) Å by neutron diffraction),<sup>22</sup>  $\text{Al}(\text{BH}_4)_3$  (1.283 (12) Å by electron diffraction),<sup>23</sup> and  $\text{B}_2\text{H}_6$  (1.339 (6) Å by electron diffraction),<sup>24,25</sup> but are somewhat longer, as might be expected,<sup>26</sup> than found in  $\text{Be}(\text{BH}_4)_2$ <sup>27</sup> by x-ray diffraction (1.18 (3) Å for nonbridging and 1.10 (4) Å for bridging tetrahydroborate groups). Unfortunately, the standard deviations of  $\text{BH}_4^-$  metrical parameters determined by x-ray diffraction for most transition metal structures are far too large to permit meaningful comparisons. These data also suffer from systematic errors.<sup>26</sup> In  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  the B–H<sub>i</sub> bond distances are essentially identical, i.e., 1.186 (16)

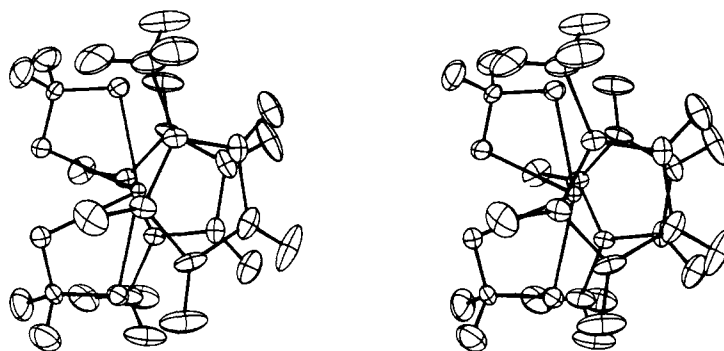


Figure 4. Stereoscopic view of the molecular structure of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ . The 50% probability vibrational ellipsoids are shown.

Table VI. Selected Bond Distances and Angles in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$

Bond Distances, Å			
Hf-H <sub>b</sub> 1	2.069 (7)	C1-C2	1.406 (7)
Hf-H <sub>b</sub> 2	2.120 (8)	C2-C3	1.407 (7)
Hf-H <sub>t</sub> 1	3.382 (11) <sup>a</sup>	C3-C4	1.411 (6)
Hf-H <sub>t</sub> 2	3.305 (11) <sup>a</sup>	C4-C5	1.382 (5)
Hf-C1	2.476 (5)	C5-C1	1.390 (5)
Hf-C2	2.456 (5)	C5-Cm	1.520 (7)
Hf-C3	2.466 (4)	C1-H1	1.028 (17)
Hf-C4	2.507 (3)	C2-H2	1.045 (15)
Hf-C5	2.550 (3)	C3-H3	1.065 (15)
Hf-RC <sup>b</sup>	2.188 (4)	C4-H4	1.056 (13)
Hf-B	2.553 (6)		
B-H <sub>b</sub> 1	1.255 (9)	Cm-H5	0.995 (18)
B-H <sub>b</sub> 2	1.208 (13)	Cm-H6	1.014 (22)
B-H <sub>t</sub> 1	1.186 (16)	Cm-H7	0.946 (26)
B-H <sub>t</sub> 2	1.198 (15)		
Bond Angles, deg			
B-Hf-B'	101.4 (3)	Hf-H <sub>b</sub> 1-B	97.3 (5)
B-Hf-RC	102.9 (2)	Hf-H <sub>b</sub> 2-B	96.3 (5)
B-Hf-RC'	109.2 (2)	H1-C1-C5	126.3 (8)
RC-Hf-RC'	128.5 (3)	H1-C1-C2	125.8 (8)
H <sub>b</sub> 1-Hf-H <sub>b</sub> 2	57.0 (3)	H2-C2-C1	127.9 (11)
H <sub>b</sub> 1-Hf-H <sub>b</sub> 1'	158.3 (4)	H2-C2-C3	124.2 (11)
H <sub>b</sub> 2-Hf-H <sub>b</sub> 2'	55.4 (5)	H3-C3-C2	125.5 (9)
H <sub>b</sub> 1-B-H <sub>b</sub> 2	108.4 (6)	H3-C3-C4	127.3 (9)
H <sub>b</sub> 1-B-H <sub>t</sub> 1	105.9 (8)	H4-C4-C3	126.8 (8)
H <sub>b</sub> 1-B-H <sub>t</sub> 2	109.3 (8)	H4-C4-C5	124.9 (8)
H <sub>b</sub> 2-B-H <sub>t</sub> 1	105.6 (9)	Cm-C5-C4	124.9 (5)
H <sub>b</sub> 2-B-H <sub>t</sub> 2	111.9 (9)	Cm-C5-C1	125.9 (5)
H <sub>t</sub> 1-B-H <sub>t</sub> 2	115.4 (10)	C5-Cm-H5	110.4 (9)
C1-C2-C3	107.9 (4)	C5-Cm-H6	110.1 (10)
C2-C3-C4	107.1(4)	C5-Cm-H7	113.9 (10)
C3-C4-C5	108.2 (4)	H5-Cm-H6	107.9 (13)
C4-C5-C1	108.9 (4)	H5-Cm-H7	106.0 (13)
C5-C1-C2	107.7 (5)	H6-Cm-H7	108.4 (15)

<sup>a</sup> Nonbonded contact. <sup>b</sup> RC = ring centroid.

and 1.198 (15) Å. These distances are nearly the same as the distances of 1.196 (12) Å in  $\text{Al}(\text{BH}_4)_3$ ,<sup>23</sup> 1.196 (8) Å in  $\text{B}_2\text{H}_6$ ,<sup>24</sup> and 1.18 (3) Å in  $\text{Be}(\text{BH}_4)_2$ .<sup>27</sup> The B-H distance obtained for  $\text{KBH}_4$  by neutron diffraction is 1.260 (2) Å.<sup>28a</sup> The angle  $\text{H}_{b1}-\text{B}-\text{H}_{b2}$  in the present structure was found to be 108.4 (6)°. This compares favorably with a value of 106 (2)° reported for  $\text{Be}(\text{BH}_4)_2$ <sup>27</sup> (nonbridging tetrahydroborate), but is larger than in  $\text{B}_2\text{H}_6$  (97.0 (3)°)<sup>24</sup> and smaller than in  $\text{Al}(\text{BH}_4)_3$  (114.0 (2)°).<sup>23</sup> The  $\text{H}_t-\text{B}-\text{H}_t$  angle is found to be greater than tetrahedral both in this work and in prior structures: 115.4 (10) (( $\text{CH}_3\text{C}_5\text{H}_5$ )<sub>2</sub> $\text{Hf}(\text{BH}_4)_2$ ), 119.0 (9) ( $\text{B}_2\text{H}_6$ ),<sup>24</sup> 127 (3) ( $\text{Be}(\text{BH}_4)_2$ ),<sup>26</sup> and 116.2 (2.2)° ( $\text{Al}(\text{BH}_4)_3$ ).<sup>23</sup>

The root-mean-square amplitudes of thermal displacement obtained from anisotropic refinement of the tetrahydroborate hydrogen atom positions in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  are significantly unequal. While  $\text{H}_{b1}(\text{H}_{b1}')$  with the shorter Hf-H<sub>b</sub>

Table VII. Best Weighted Least-Squares Planes for  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  Cyclopentadienyl Rings<sup>a</sup>

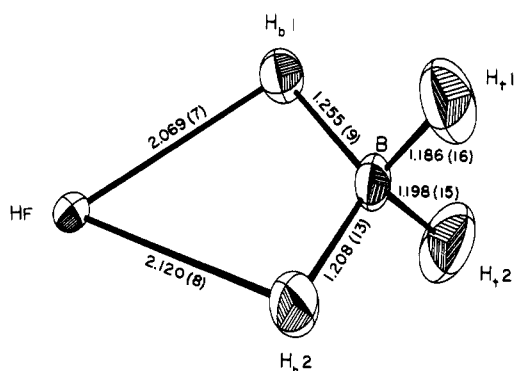
C1	-0.023 (4)	H1	-0.003 (10)
C2	0.013 (4)	H2	0.037 (10)
C3	0.004 (4)	H3	0.034 (11)
C4	-0.014 (4)	H4	-0.005 (10)
C5	0.013	Cm	0.226 (8)

<sup>a</sup> Equation  $0.8850x + 0.4645y - 0.324z = 1.459$ . Deviations of atoms from best plane are given in Å.

distances exhibits relatively small and isotropic thermal ellipsoid principal axes, i.e., 0.252 (9), 0.258 (9), and 0.319 (8) Å, hydrogen atoms  $\text{H}_{b2}(\text{H}_{b2}')$ ,  $\text{H}_{t1}(\text{H}_{t1}')$ , and  $\text{H}_{t2}(\text{H}_{t2}')$  exhibit considerably greater anisotropy, viz., 0.234 (10), 0.260 (12), and 0.462 (12) Å; 0.265 (13), 0.380 (13), and 0.442 (13) Å; 0.248 (13), 0.368 (13), and 0.517 (15) Å, respectively. The direction of greatest hydrogen ellipsoid elongation is approximately perpendicular to the B-H bond vectors, as can be seen in Figure 3. The boron atom root-mean-square amplitudes are also somewhat anisotropic: 0.194 (8), 0.250 (8), and 0.360 (7) Å.

## Discussion

The precise definition and the nature of the  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  molecular structure provide new insight into the properties of this particular complex and possibly into certain general characteristics common to transition metal tetrahydroborate compounds. On incorporation into diborane and involvement in three-center two-electron bonding,<sup>29</sup> the  $\text{BH}_4^-$  skeleton undergoes several pronounced structural changes: lengthening of the B-H<sub>b</sub> bonds, shortening of the B-H<sub>t</sub> bonds, closing of the  $\text{H}_b-\text{B}-\text{H}_b$  angle, and opening of the  $\text{H}_t-\text{B}-\text{H}_t$  angle.<sup>24</sup> This major reorganization is evident in  $\text{B}_2\text{H}_6$  vibrational spectra.<sup>3a,30</sup> It is clear from the present neutron diffraction structural work that the corresponding changes in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  are not so great, although the modifications which can be observed are in the anticipated direction. Both B-H<sub>t</sub> bond shortening and  $\text{H}_t-\text{B}-\text{H}_t$  angle increase are found (Table VI). However, the observed perturbation within the  $\text{B}(\text{H}_b)_2$  framework is minimal. Such a result is in qualitative agreement with the  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  vibrational spectra, which exhibit a smaller perturbation from free  $\text{BH}_4^-$  than is observed in diborane<sup>30</sup> and in most other transition metal complexes;<sup>3a,5</sup> i.e., for  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ , stronger B-H<sub>b</sub> and weaker M-H<sub>b</sub> interactions than usual<sup>3a</sup> are detected. Also in concurrence with these observations, the molecular orbital calculations of Lauher and Hoffmann<sup>6</sup> show that in the idealized  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$  structure having all four bridging hydrogen atoms coplanar, one of the four donor molecular orbitals ( $b_2$ ) provided by the two tetrahydroborate groups does not possess the correct symmetry for bond formation with, and electron donation to, the  $(\text{C}_5\text{H}_5)_2\text{Zr}$  center. It is likely that this reduced metal-ligand bonding persists to



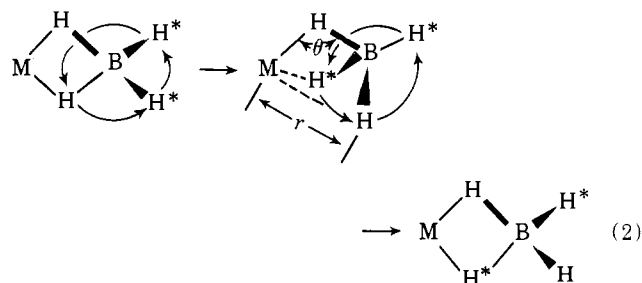
**Figure 5.** Summary of bond distances in the coordinated tetrahydroborate ligand. The 50% probability vibrational ellipsoids are shown.

a significant degree in the actual  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  molecular geometry. It should be noted, however, that the present structural results do give some indications of multicenter electron-deficient bonding in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ . In particular, the apparent inverse relationship of B-H<sub>b</sub> and Hf-H<sub>b</sub> distances is in accord with such a model. Whether such trends and the departure from free  $\text{BH}_4^-$  metrical parameters will be even greater in the more "boranelike" transition metal complexes, which exhibit far greater  $\text{BH}_4^-$  reorganization in the vibrational spectra, remains to be determined.

In regard to the stereochemical configuration of the two tetrahydroborate groups about the  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}^{2+}$  framework, several observations are noteworthy. First, the crowding which is necessary to accommodate two bidentate ligands (witness the large H<sub>b</sub>1-Hf-H<sub>b</sub>1' bond angle) has not induced any perceptible distortion of the ring-Hf-ring geometry.<sup>10a,19</sup> The exact placement of the  $\text{BH}_4^-$  ligands appears to reflect both the nonbonded repulsions (both ring- $\text{BH}_4^-$  as well as  $\text{BH}_4^-$ - $\text{BH}_4^-$ ) already noted in the structural discussion as well as molecular orbital considerations. In this regard, the calculations of Lauher and Hoffmann<sup>6</sup> show that the tetrahydroborate  $b_2$  molecular orbital not only has the incorrect symmetry to interact with the metal, hence weakening metal-ligand bonding, but that this orbital is antibonding between the two bridging hydrogens which correspond to H<sub>b</sub>2 and H<sub>b</sub>2' in the present structure. This observation is a further reason for the observed twisting of the tetrahydroborate groups and the apparent repulsive interaction between these two atoms.

It is evident from the NMR spectral studies that the bridge-terminal hydrogen interchange process in  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  is exceedingly rapid, even at  $-155^\circ\text{C}$ . Treating this process as a two-site exchange process (which, as will be seen, is a simplification) and using the chemical shift of the terminal hydrogen atoms in  $\text{Mo}(\text{CO})_4\text{BH}_4^-$ <sup>11a</sup> ( $\delta$  4.3 ppm) together with the average shift of all four  $\text{BH}_4^-$  hydrogen atoms from the present work, it is possible to calculate an approximate chemical shift separation between the exchanging sites, 5.5 ppm. Assuming that at  $-155^\circ\text{C}$  and 90 MHz the spectral coalescence point has not been reached, then the modified Bloch equation for coalescence<sup>31</sup> combined with the standard relationship between rate and free energy of activation<sup>32</sup> indicate that  $\Delta G^\ddagger \leq 4.9$  kcal/mol. Reference to the molecular structure of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  (Figure 3) indicates that all four tetrahydroborate protons are magnetically nonequivalent. In terms of nuclear permutation processes,<sup>33</sup> the lower  $C_1$  symmetry in the present case dictates that there will be a greater number of rearrangements which are theoretically differentiable by NMR than for the  $C_{2v}$  (A) structure,<sup>3a,11a</sup> i.e., 24 instead of 3.<sup>34</sup> Of these 24 reactions,<sup>34b</sup> 18 including the identity operation do not involve permutation of all four nuclear sites and could not, alone, give rise to a single hydrogen resonance at fast exchange. Though the rate of the

dynamic process was too rapid to yield mechanistic information in solution,<sup>35</sup> the neutron diffraction study reveals an interesting result which may be relevant to the bridge-terminal hydrogen atom permutation pathways. As can be readily appreciated in Figure 3 and was already noted above, the structure refinement revealed highly anisotropic root mean square displacement amplitudes for hydrogen atoms H<sub>b</sub>2(H<sub>b</sub>2'), H<sub>t</sub>1(H<sub>t</sub>1'), and H<sub>t</sub>2(H<sub>t</sub>2') compared to the results for H<sub>b</sub>1(H<sub>b</sub>1'). The directions of maximum displacement suggest that a rather flat potential energy surface may exist for oscillation of the ligand about the B-H<sub>b</sub>1 (or B-H<sub>b</sub>1') bond axis. From the boron atom thermal parameters it appears that a similar (or correlated) situation may also exist for ligand rocking about the Hf-H<sub>b</sub>1 bond axis. Permutational processes of type (H<sub>t</sub>1H<sub>b</sub>2H<sub>t</sub>2)(H<sub>b</sub>1) can be identified with the "concerted" reaction pathway previously discussed for bidentate tetrahydroborates<sup>3a,11a</sup> and illustrated in eq 2. Though motions



about the B-H<sub>b</sub>1 axis such as (H<sub>t</sub>1H<sub>b</sub>2H<sub>t</sub>2)(H<sub>b</sub>1) do not suffice to permute all four spins, it is reasonable to suppose that the longer and presumably weaker H<sub>b</sub>2-Hf bond would permit the greatest motional excursions along this coordinate. A second process, also of very low activation energy, would then be required to involve H<sub>b</sub>1 in the hydrogen atom exchange. Analogous oscillation of coordinated tridentate tetrahydroborate about the threefold M-B-H<sub>t</sub> axis has been observed in broad-line NMR studies of solid  $\text{Hf}(\text{BH}_4)_4$ .<sup>36</sup> In this case also, rather large thermal parameters along this coordinate were observed in structural studies.<sup>21,37</sup>

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**Supplementary Material Available:** Structure factors for  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$  (6 pages). Ordering information is given on any current masthead page.

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## Reduction of Carbon Monoxide Promoted by Alkyl and Hydride Derivatives of Permethylyirconocene

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**Abstract:** Bis(pentamethylcyclopentadienyl)dihydrozirconium(IV), ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub> (**2**) is prepared by the reaction of H<sub>2</sub> with {( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrN<sub>2</sub>}<sub>2</sub>N<sub>2</sub> (**1**). **2** forms unstable adducts with PF<sub>3</sub> and CO at –80 °C. The carbonyl adduct ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub>(CO) yields {( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub>(OCH=CHO)} and/or ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH(OCH<sub>3</sub>), depending on reaction conditions. Carbonylation of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>), obtained from ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> and methylithium, yields successively ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)(CH<sub>3</sub>CO) and ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(O(CH<sub>3</sub>)C=C(CH<sub>3</sub>)O). The zirconacyclopentane complex ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>) (**10**) is prepared from **1** and ethylene. Carbonylation of **10** affords ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(OC=CH(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>). Treatment of **2** with isobutylene yields ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(CH<sub>2</sub>CHMe<sub>2</sub>) (**13**), which undergoes a reaction with CO to form ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(OCH=CHCHMe<sub>2</sub>) (**15**). The results of <sup>13</sup>C and deuterium labeling studies indicate that the conversion of **13** to **15** is mediated by ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(Me<sub>2</sub>CHCH<sub>2</sub>CO). The observed patterns for these reactions of alkyl and hydride derivatives of zirconium with CO are attributed to carbenoid character of the carbonyl carbon resulting from an unusual "side-on" coordination of acyl and formyl groups.

### Introduction

The development of homogeneous catalysts for selective conversion of CO and H<sub>2</sub> to alkanes or alcohols is a problem of growing interest. Homogeneous systems thus far reported to catalyze the reduction of CO by H<sub>2</sub> include the Rh-based ethylene glycol synthesis,<sup>2</sup> methanation promoted by Os<sub>3</sub>(CO)<sub>12</sub> or Ir<sub>4</sub>(CO)<sub>12</sub>,<sup>3</sup> and most recently the catalytic

production of methane, ethane, propane, and isobutane by Ir<sub>4</sub>(CO)<sub>12</sub> in molten NaCl·2AlCl<sub>3</sub>.<sup>4</sup>

We recently reported that H<sub>2</sub> stoichiometrically reduces ligated CO in certain carbonyl compounds of zirconium:<sup>5</sup>

