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Gas-Phase Molecular Structure of (η^5-C_5H_5)Zr(BH_4)$_3$: Electron-Diffraction and EHMO Study

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(C_5H_5)Zr(BH_4)$_3$ has been synthesized in excellent yield from (C_5H_5)ZrBr_3 and LiBH_4 and its molecular structure in the gas phase determined by electron diffraction at a nozzle temperature of 115 °C. The results were interpreted in terms of an η^5-C_5H_5 group and a trigonal-pyramidal arrangement of boron atoms around Zr. The infrared spectrum clearly indicates triple hydrogen bridges between the borohydride groups and the zirconium atom; the diffraction data are fit about equally well by either double- or triple-bridge models. There is some inferential evidence in the values of the parameters, however, that suggests the triple-bridge model to be the more likely. Values of some of the bond distances (r_a/Å) and bond angles ($\angle_a$/deg) with estimated 2σ uncertainties for the triple-bridge model (C_{3v} local symmetry assumed for the BH_4 groups) are r(Zr–B) = 2.403 (29), r(Zr–C) = 2.519 (18), r(Zr–H_b) = 2.197 (28), r(C–C) = 1.418 (2), r(B–H_b) = 1.236 (58), r(B–H_t) = 1.217 (114), $\angle$Q–Zr–B (Q is the center of the cyclopentadienyl ring) = 115.0 (10), $\angle$B–Zr–B = 103.4 (12), $\angle H_b$–B–H_b = 103.9 (19), and $\angle H_b$–B–H_t = 114.6 (16). Finally, EHMO calculations are presented which support the idea that the triply bridged borohydride group can be considered to be isolobal with the η^5-C_5H_5 ligand.

Introduction

In nuclear power generation there are considerable economic advantages to be derived from the use of zirconium enriched in a low cross section isotope. Thus, use of ^{90}Zr in the pressure and calandria tubes of a generating station would bring about increased neutron economy obtained by minimizing the parasitic neutron loss because of absorption in the reactor materials. To this end, much effort has been directed toward the synthesis of volatile complexes of zirconium possessing vibration frequencies in the range of a cheap, efficient laser. The known volatility of Zr(BH_4)$_4$ prompted us to prepare other zirconium borohydrides with a view to assessing their suitability for laser isotope separations. These molecules also raise interesting questions about the bonding interactions between zirconium and the borohydride ligands.

The structures of inorganic and organometallic derivatives of tetrahydroborates, $L_xM(BH_4)_y$, have received much attention in recent years. A large part of this attention has been focused on the bonding that links the metal atoms and the BH_4 groups. This occurs in the form of three or two (or, rarely, one) hydrogen bridges per ligand; examples are compounds of metals such as Be, Al, Sc, Ti, Co, Cu, Ga, Y, Zr, Nb, Mo, Hf, U, and Np.[2] Determination of the hydrogen-bridge order rests principally on the experimental method of X-ray diffraction. Electron diffraction and neutron diffraction have also been used, and there is evidence[3] that in some cases the vibrational spectra of bi- and tridentate (two- and three-bridge) groups differ enough in the B–H stretching region to permit their identification. It has also been shown[4,5] that the number of bridging hydrogens from each BH_4 group can be correlated with the number of vacant orbitals of suitable energy and symmetry on the metal atom.

Although it has been possible to distinguish bi- and tridentate BH_4 hydrogen bridges in many compounds by diffraction techniques, the determination is often difficult in the presence of metals because of the low scattering power of hydrogen atoms for X-rays and electrons. Bernstein et al.[6] have suggested that conclusions about the bridging could be drawn from the value of the M–B distance (which for a given metal ion tends to be longer in bidentate structures than in tridentate ones), and the relation between effective ionic radii and M–B distances in structures known to have one or the other type of BH_4 bonding has been explored.[2,6,7]

Results from vibrational spectroscopy,[8] electron diffraction,[9] and X-ray crystallography[10] all agree that in Zr(BH_4)$_4$, which has tetrahedral symmetry, three hydrogen atoms bridge the zirconium atom and each boron atom. Substitution of the BH_4 ligands with cyclopentadienyl groups leads to molecules with vibrational spectra characteristic of triple bridges for (C_5H_5)Zr(BH_4)$_3$ and double bridges for (C_5H_5)$_2$Zr(BH_4)$_2$, as shown in Figure 1.[11] The conclusions about the order of the hydrogen bridging in these molecules (for which direct structural measurements apparently do not exist) struck us as interesting, and we decided to undertake an electron-diffraction investigation of the monocyclopentadienyl derivative (Figure 2). We knew that it would be difficult to measure the number of bridging hydrogens reliably, not only because of the low scattering power of hydrogen but also because the many distances arising from the cyclopentadienyl group complicate the structural picture substantially. Nevertheless, we expected to be able to measure the principal parameters including the Zr–B distance, and with use of values for the ionic radii of the metal and of doubly and triply bridged BH_4 groups derived by Edelstein,[2] we hoped to obtain strong inferential evidence about the bridging.

Experimental Section

Synthesis of (C_5H_5)Zr(BH_4)$_3$. All manipulations were carried out either under an atmosphere of dry nitrogen or by using high vacuum techniques, and solvents were dried carefully before use. ^{1}H and ^{11}B NMR spectra were obtained on a Bruker WM 250-MHz spectrometer operated respectively at 250 and 80.21 MHz; boron-11 shifts are quoted relative to BF_3·EtO. Gas-phase infrared spectra were obtained by using a cell that could be heated to 85 °C. Microanalytical data are from Guelph Analytical Laboratories, Guelph, Ontario.

Cyclopentadienylthallium (5.0 g, 18.6 mmol), which had been freshly prepared and sublimed under vacuum at 120 °C, was added to zirconium tetrabromide (9.0 g, 21.9 mmol) in dry benzene (70 mL). The mixture was heated under reflux in a stream of dry nitrogen for 1 h, after which time the solvent was removed under reduced pressure. Vacuum sublimation at 175–200 °C gave (C_5H_5)ZrBr_3 (6.41 g, 16.2 mmol; 87%) as pale yellow crystals, which were readily characterized by mass spectrometry. Analogously, (C_5H_5)ZrCl_3 was also prepared in excellent yield.

Lithium borohydride (0.45 g, 20.7 mmol) and (C_5H_5)ZrBr_3 (2.0 g, 5.05 mmol) in dry benzene (10 mL) were stirred at room temperature for 3 h, by which time the initially pale yellow solution had become colorless. After filtration and removal of the solvent in vacuo, the product was purified by sublimation at 35–40 °C/0.1 Torr to yield colorless

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(1) (a) Oregon State University. (b) On leave from Eötvös Loránd University, Budapest, Hungary. (c) McMaster University.

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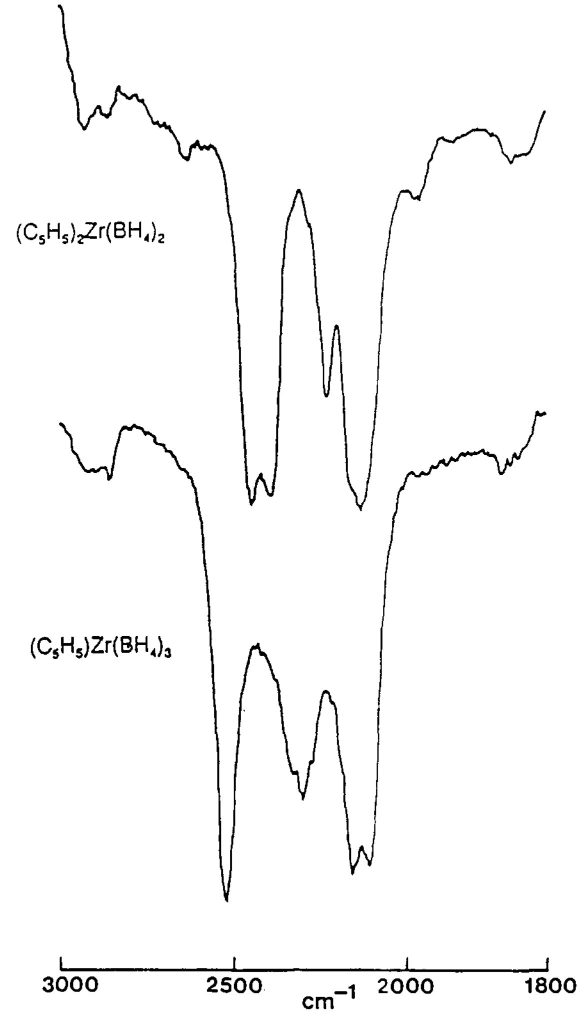

Figure 1. Infrared spectra (in benzene solution) of $(C_5H_5)_2Zr(BH_4)_2$ and of $(C_5H_5)Zr(BH_4)_3$ in the B-H stretching region.

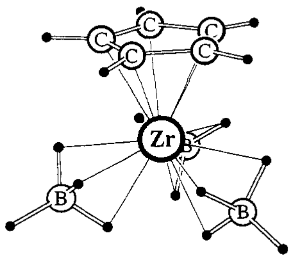

Figure 2. Diagram of the molecule.

crystals of $(C_5H_5)Zr(BH_4)_3$ (0.96 g, 4.8 mmol; 95%). ^1H NMR (C_6D_6): δ 5.8 (5 H, singlet), 1.54 ppm (12 H, 1:1:1:1 quartet, J_{B-H} = 91 Hz). ^{11}B NMR: δ −11.2 ppm (1:4:6:4:1 quintet). Infrared spectra (ν_{B-H} stretching vibrations): C_6H_6 solution 2520 (s), 2158 (s), and 2110 cm^{-1} (s); gas phase 2536 (s), 2156 (s), and 2111 cm^{-1} (s); Nujol mull 2530 (s), 2155 (s), and 2100 cm^{-1} (s). Raman spectra: solid state 2530 (s), 2156 (m), and 2110 cm^{-1} (w). The corresponding ν_{B-D} infrared vibrations in the borodeuteride, $(C_5H_5)Zr(BD_4)_3$, appeared at 1899 (s), 1580 (w), and 1538 cm^{-1} (s) in the gas phase and at 1893 (s), 1578 (w), and 1549 (s) cm^{-1} in the Raman spectrum. Anal. Calcd for $C_5H_{17}B_3Zr$: C, 29.90, H, 8.53; B, 16.15. Found: C, 30.04; H, 8.49; B, 16.28.

Electron-Diffraction Experiments. The purity of the sample used for the electron-diffraction study was estimated to be greater than 99%. The diffraction data were obtained with the Oregon State apparatus operated under the following conditions: sector shape, r^3; plates, 8 in. × 10 in. Kodak projector slide medium contrast; development, 10 min in D-19, diluted 1:1; nominal nozzle-to-plate distances, 750 mm (long camera) and 300 mm (middle camera); nominal electron wavelength, 0.058 Å (calibrated in separate experiments with CO_2: $r_a(C{=}O)$ = 1.1646 Å and $r_a(O{\cdot}O)$ = 2.3244 Å); exposure times, 100–240 s; beam currents, 0.3–0.4 mA; ambient pressure during experiments, (3–4) × 10^{-6} Torr; nozzle temperature, 115 °C.

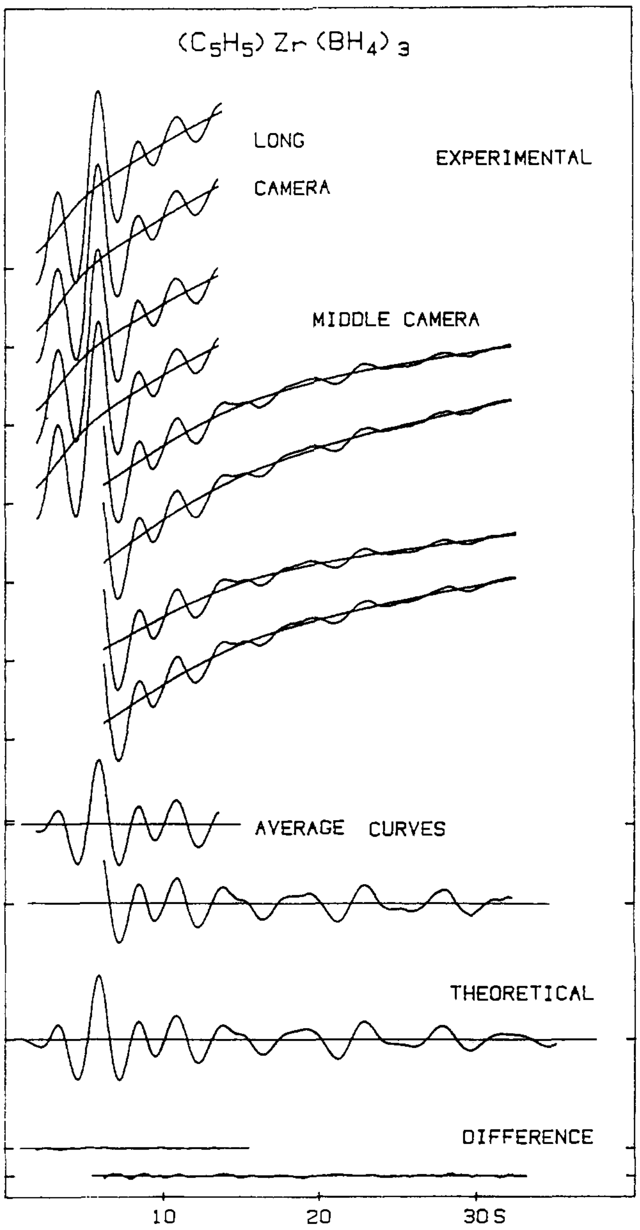

Figure 3. Intensity curves for cyclopentadienylzirconium tetrahydroborate. The s^4I_t experimental curves are shown magnified 5 times with respect to the backgrounds on which they are superimposed. The average curves are $s(s^4I_t$ − bkgd). The theoretical and difference curves are for the tridentate model of Table I.

To obtain sufficient vapor pressure for our experiments, it was necessary to heat the sample to 103 °C. Following the experiments, it was evident from a dark deposit in the sample tube that some decomposition had taken place. However, the cold trap (one that surrounds the gas nozzle and condenses the sample immediately after it passes the scattering region) was coated with a white material of uniform appearance. This material was still present 18 h later after the trap had warmed up, a behavior consistent with that of the original material. The possible volatile decomposition products are B_2H_6 and $Zr(BH_4)_4$, for which electron scattering data are available.[9,12]

Four plates from each camera distance were selected for analysis. The ranges of intensity data were 2.00 ≤ s/Å^{-1} ≤ 13.75 (long camera) and 6.50 ≤ s/Å^{-1} ≤ 32.25 (middle camera); the data interval was Δs = 0.25 Å^{-1} for both distances. The usual procedures[13,14] for obtaining the total scattered intensities ($s^4I_t(s)$) and molecular intensities ($sI_m(s)$) were followed. Curves of the intensity data superimposed on their comput-

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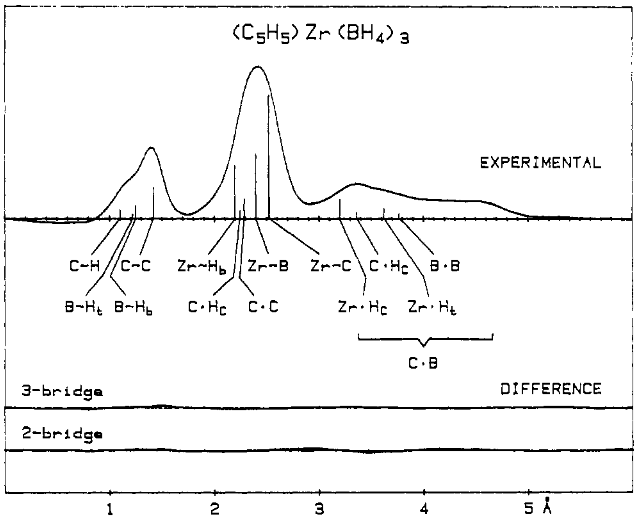

Figure 4. Radial distribution curves for cyclopentadienylzirconium tetrahydroborate. The experimental curve was calculated from a composite of the average intensities with use of theoretical data for the region $0 \leq s/\text{Å} \leq 2.00$ and $B/\text{Å}^2 = 0.0025$. The vertical lines have lengths proportional to weights of the indicated distances.

er-generated backgrounds are shown in Figure 3; the data are available as supplementary material. Figure 4 shows the final radial distribution curve ($rD(r)$) calculated in the usual way[13a] from the modified molecular intensity $I'(s) = sI_m(s)Z_{Zr}Z_CA_{Zr}^{-1}A_C^{-1}\exp(-Bs^2)$, where $A = s^2F$ and F is the complex electron-scattering amplitude.[15] Data in the unobserved region $s < 2.00$ Å^{-1} were taken from theoretical curves, and all the amplitudes and phases were taken from tables.[15]

Theoretical Calculations. All calculations were carried out within the extended Hückel formalism[16,17] using the weighted H_{ij} formula.[18] The atomic parameters for zirconium were taken from ref 19. Structural parameters for $Zr(BH_4)_4$ were taken from ref 9. In the case of $(\eta^5\text{-}C_5H_5)Zr(\eta^3\text{-}BH_4)_3$, a borohydride moiety was removed from $Zr(BH_4)_4$ and a cyclopentadienyl ring was placed at a zirconium-to-ring centroid distance of 2.21 Å, as found by electron diffraction. All C–C distances were taken as 1.42 Å.

Structure Analysis

Models and Refinements. The radial distribution curve shows little resolution of even the more important terms in $(C_5H_5)Zr(BH_4)_3$ and thus provides almost no help toward the construction of trial structures for refinement. We drew on data from other molecules for this purpose and carried out many tests to establish the suitability of model types that eventually became the basis of our investigation.

Although the barrier to interconversion of η^1 and η^5 bonding in C_5H_5M compounds can be quite small,[5,20] the vibrational spectra of $(C_5H_5)_2Zr(BH_4)_2$[11] (and $(C_5H_5)Zr(BH_4)_3$) hold no suggestion of deviation of the C_5H_5Zr part of the molecule from local C_{5v} symmetry. Various tests showed our diffraction data to be consistent with the spectroscopic observations, and local C_{5v} symmetry for this group was assumed for all models. The C_5H_5 group itself was assigned D_{5h} symmetry when it was found that displacements of the hydrogen atoms from the plane of the carbon ring could not be detected. Other tests revealed that a reversal of the relative magnitudes of the presumed shorter Zr–B and longer Zr–C distances (r(Zr–B) = 2.31 Å in $Zr(BH_4)_4$;[9] r(Hf–C) = 2.49 Å in $(MeC_5H_4)_2Hf(BH_4)_2$[21]) results in poorer fits; r(Zr–B) < r(Zr–C) was assumed in the final refinements. Models that represented both bi- and tridentate bonding of the BH_4 groups in $(C_5H_5)Zr(BH_4)_3$ were designed. With the assumptions described above, 10 structural parameters are needed for the specification of the bidentate model. Those chosen were the bond distances r(Zr–B), r(C–C), and r(C–H); the average of $r(B\text{–}H_b)$ and $r(B\text{–}H_t)$ ($\langle r(B\text{–}H)\rangle = (r(B\text{–}H_b) + r(B\text{–}H_t))/2$) and their differences ($\Delta r(B\text{–}H) = r(B\text{–}H_t) - r(B\text{–}H_b)$); and the distance between the Zr atom and the centroid of the cyclopentadienyl ring (Zr–Q). The other parameters were the angles ∠Q–Zr–B, $\angle Zr\text{–}B\text{–}H_b$, and $\angle H_t\text{–}B\text{–}H_t$ and the angle of rotation of the BH_4 group around the Zr–B bond (τ). The $ZrBH_4$ groups were assigned C_{2v} symmetry. With elimination of the angle $\angle H_t\text{–}B\text{–}H_t$, a redefinition of $\langle r(B\text{–}H)\rangle$ [$= (3r(B\text{–}H_b) + r(B\text{–}H_t))/4$], and assumptiion of C_{3v} symmetry for the $ZrBH_4$ groups, this parameter set also served for the tridentate models.

Table I. Structural Results for $(C_5H_5)Zr(BH_4)_3$[a,b]

	tridentate model		bidentate model	
parameter	r_a, $\angle_a$	l	r_a, $\angle_a$	l
	Structure-Defining Parameters			
r(C–H)	1.105 (25)	0.085 (26)[c]	1.099 (20)	0.081 (22)[c]
r(C–C)	1.418 (2)	0.051 (3)	1.418 (2)	0.051 (3)
$\langle r(B\text{–}H)\rangle$	1.232 (23)		1.228 (28)	
Δr(B–H)	0.019 (168)		0.020 (219)	
r(Zr–Q)	2.212 (20)		2.175 (5)	
r(Zr–B)	2.403 (29)	0.085 (30)	2.398 (26)	0.088 (29)
∠(Q–Zr–B)	115.0 (10)		117.9 (17)	
$\angle(Zr\text{–}B\text{–}H_b)$	65.4 (16)		65.7 (51)	
$\tau(BH_4)$	[60.0][d]		[30.0][d]	
	Other Parameters			
∠B–Zr–B	103.4 (12)		99.9 (21)	
$\angle(H_b\text{–}B\text{–}H_b)$	103.9 (19)		131.5 (104)	
$\angle(H_b\text{–}B\text{–}H_t)$	114.6 (16)		104.5 (30)	
$\angle(H_t\text{–}B\text{–}H_t)$			[105.0]	
$r(B\text{–}H_b)$	1.236 (58)	0.100 (26)[c]	1.249 (76)	0.096 (22)[c]
$r(B\text{–}H_t)$	1.217 (114)	0.090 (26)[c]	1.215 (44)	0.086 (22)[c]
$r(Zr\text{–}H_b)$	2.197 (28)	0.161 (33)	2.156 (24)	0.128 (28)
r(Zr–C)	2.519 (18)	0.091 (14)	2.514 (16)	0.091 (11)
r(C·C)	2.295 (3)	0.059 (5)	2.294 (3)	0.059 (4)
r(B·B)	3.772 (47)	0.150 (95)	3.703 (43)	0.126 (31)
$r(C\cdot H_C)$	2.253 (24)	[0.090]	2.248 (17)	[0.090]
$r(C\cdot\cdot H_C)$	3.363 (27)	[0.100]	3.357 (19)	[0.100]
$r(Zr\cdot H_C)$	3.199 (26)	0.168 (52)[e]	3.191 (15)	0.216 (35)[e]
$r(Zr\cdot H_t)$	3.620 (112)	0.128 (52)[e]	3.283 (45)	0.216 (35)[e]
$r(C\cdot B)_{syn}$[f]	{3.4–3.9}	0.185 (106)	{3.4–4.0}	[0.180]
$r(C\cdot B)_{anti}$[f]	{4.0–4.7}	0.114 (32)	{4.1–4.7}	0.121 (35)
$r(B\cdot\cdot H_B)$	{3.1–4.8}	[0.230]	{3.1–4.8}	[0.230]
$r(C\cdot\cdot H_B)$	{2.7–5.8}	[0.210]	{2.6–5.8}	[0.210]
$r(B\cdot\cdot H_C)$	{3.2–5.5}	[0.200]	{3.2–5.5}	[0.200]
$X(B_2H_6)$[g]	0.05 (7)		[0.0]	
R[h]	0.051		0.051	

[a] Distances (r) and amplitudes (l) in angstroms; angles (∠) in degrees. Quantities in parentheses are estimated 2σ; those in square brackets are assumed. [b] Distances in curly brackets denote a range of distances reflecting rotation of the C_5H_5 group. See text. [c] Refined as a group. [d] Zero of τ is the eclipsed conformation of the $B\text{–}H_b$ bond and the Zr–Q vector. [e] Refined as a group. [f] Syn and anti refer to locations of groups of carbon atoms in the rotating C_5H_5 group relative to boron atoms. [g] Mole fraction of diborane assumed to be an impurity. [h] $R = [\sum_i w_i\Delta_i^2/\sum_i w_i(s_iI_i(\text{obsd}))^2]^{1/2}$, where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

There are a large number of vibrational amplitude parameters. For both models the individually refinable amplitudes were those associated with the Zr–B, Zr–C, $Zr\text{–}H_b$, C–C, B·B, and C·C distances. The amplitudes of the two different C·H(C) distances were fixed at values taken from nickelocene.[22] Other amplitudes were grouped and refined as one parameter; the groupings are evident from Table I. A special arrangement was adopted for the C_5H_5 group, which is known to rotate quite freely in similar molecules. Such large amplitude motion in $(C_5H_5)Zr(BH_4)_3$ could not be represented satisfactorily by the usual frame-vibration approach. We simulated this motion by positioning 10 C–H groups, each with half the normal weight, at 36° intervals around the circle of rotation and refined frame amplitudes for the more important terms generated by each of these.

Refinements were done by least squares[14] that fitted a theoretical intensity curve to the two experimental ones obtained by averaging the data from the plates made at the two camera distances. All terms except those for the nonbond $H_C\cdot H_B$ were included in the intensity calculations. Because of the large amplitude motion associated with rotation of the

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Table II. Correlation Matrix (×100) for Parameters for the Three-Bridge Model of $(C_5H_5)Zr(BH_4)_3$[a]

	σ_{LS}[b]	r_1	r_2	r_3	r_4	r_5	r_6	r_7	$\angle_8$	$\angle_9$	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	X_{15}
r(C–H)	0.99	100														
r(C–C)	0.054	−30	100													
r(B–H_b)	2.1	−49	23	100												
r(B–H_t)	4.0	17	−9	−89	100											
r(Zr–C)	0.63	12	2	29	−31	100										
r(Zr–B)	1.0	1	−18	−22	18	−89	100									
r(Zr–H_b)	1.0	−30	4	−30	42	−5	13	100								
∠(Q–Zr–B)	36.0	−26	−2	−2	9	−27	27	4	100							
∠(H_b–B–H_t)	56.0	16	−13	−7	−3	−66	64	−66	18	100						
l(C–H)	0.90	83	−20	27	−63	20	−9	−36	−23	12	100					
l(C–C)	0.069	33	−18	−4	−19	−3	5	−45	9	38	41	100				
l(Zr–C)	0.48	−13	−15	−23	24	−91	95	7	33	67	−21	10	100			
l(Zr–B)	1.0	−8	3	−27	28	−98	84	4	28	62	−18	7	89	100		
l(Zr–H_b)	1.2	−56	11	−20	42	−53	23	6	29	19	−62	−7	46	57	100	
X[c]	7.3	−14	−28	18	2	−13	13	2	15	8	−49	−9	23	17	42	100

[a] Distances (r) and amplitudes (l) in angstroms; angles (∠) in degrees. [b] Standard deviations (×100) from least squares. [c] Mole fraction of diborane impurity.

C_5H_5 group, shrinkage corrections were regarded to be of no consequence and were ignored. Tests showed, as expected, that no information could be obtained about the torsion angles τ. With $\tau = 0°$ taken as an eclipsed conformation of one of the B–H_b bonds and the Zr–Q vector, these angles were set at 30° in the bidentate model and at 60° in the tridentate. (Angles appreciably different from these led to unreasonably close approach of the BH_4 hydrogens to hydrogens either on the carbons or on other BH_4 groups.) Tests also showed that inclusion of the hypothetical decomposition product $Zr(BH_4)_4$[9] in the models worsened the fit, and accordingly, this impurity was disregarded in the final calculations. Allowance was made for the presence of the other decomposition product, B_2H_6, in the sample, but little or no change in the values of the refined parameters occurred.

Results

The final results are listed in Table I for the bi- and tridentate models. Although an attempt was made to refine each under similar conditions, it was necessary to modify the bidentate model in several ways to avoid failure of convergence or to interrupt the generation of bizarre values for some of the parameters. Thus, the parameter $l(C\cdot B)_{syn}$ had to be removed from the refinable list, and the mole fraction of the B_2H_6 impurity had to be set to zero. The better behavior of the tridentate model leads us to prefer it to the bidentate. We emphasize, however, that each of the models, as defined by the parameters of Table I, give good fits to the diffraction data and cannot be rejected on experimental grounds alone.

Table II is the correlation matrix for the more important parameters of the tridentate model.

Discussion

Synthesis and Vibrational Spectroscopy. At the outset of this investigation, the known borohydrides of zirconium were $Zr(BH_4)_4$,[23] $(C_5H_5)_2Zr(BH_4)_2$,[24] and $(C_5H_5)_2Zr(H)BH_4$;[25] the pentamethylated derivatives $(C_5Me_5)Zr(BH_4)_3$ and $[(C_5Me_5)Zr(H)(BH_4)(\mu\text{-}H)]_2$ were reported subsequently.[26] Routes to complexes of the type $(C_5H_5)ZrL_3$ were difficult, since no convenient preparation of $(C_5H_5)ZrCl_3$ was available; this molecule had been prepared either photochemically (en route to $(C_5H_5)ZrPh_3$)[27] or via the reaction of $ZrCl_4$ with $(C_5H_5)_2Mg$,[28] but neither method gives good yields reliably. We have circumvented this problem by using $(C_5H_5)Tl$ as the source of the cyclopentadienyl moiety; this approach routinely gives excellent yields of $(C_5H_5)ZrX_3$, where X = Cl or Br, in multigram quantities. Subsequent reaction with $LiBH_4$ (or $LiBD_4$) gives the desired products almost quantitatively.

The spectroscopic criteria used to differentiate doubly and triply bridged borohydride ligands have been discussed in some detail by Marks et al.[3] It has been shown that the former give rise to a strong doublet in the infrared spectrum ($A_1 + B_1$) in the 2400–2600-cm^{-1} region attributable to B–H_t vibrations and a singlet (possibly with a shoulder) for B–H_b vibrations at 1650–2100 cm^{-1}. In contrast, triply bridging ligands have but a single B–H_t environment and so yield a strong singlet at 2450–2600 cm^{-1}; concomitantly, the three B–H_b bonds should give rise to a strong doublet (A_1 + E) in the range 2100–2200 cm^{-1}. Figure 1 shows the infrared spectra in the B–H stretching region of $(C_5H_5)_2Zr(BH_4)_2$ and of $(C_5H_5)Zr(BH_4)_3$. These data clearly indicate that in benzene solution the bis(borohydride) complex has bidentate BH_4^- ligands while in the tris(borohydride) system the ligands are attached in a tridentate manner. Moreover, the gas-phase IR spectra of $(C_5H_5)Zr(BH_4)_3$ and $(C_5H_5)Zr(BD_4)_3$ also show the singlet B–$H(D)_t$ and doublet B–$H(D)_b$ absorptions in accord with the triply bridged formulation. The ^1H and ^{11}B NMR spectra are entirely typical of fluxional borohydride systems in terms of peak multiplicities, chemical shifts, and coupling constants. The rapid interconversion of terminal and bridging hydrogen environments is reflected in a 1:4:6:4:1 quintet for the ^{11}B resonance and a 1:1:1:1 quartet for the proton signal. This peak pattern is unchanged even at −90 °C and does not permit one to distinguish between double- or triple-bridge structures.

Molecular Structure. One of the objects of our diffraction study was to obtain corroborative evidence for the order of the bonding, not by a direct determination of the number of bridging hydrogen atoms, which was an unlikely possibility, but by an accurate measurement of the Zr–B distance, which has been shown[2,6] to be correlated with the number of bridging hydrogens. As described above, our results do not provide a direct measurement of the number of bridging hydrogens. Unfortunately, neither do they permit a clear choice based on the Zr–B distance criterion, as the following considerations show. According to Edelstein,[2] the norm for these distance types in $(C_5H_5)Zr(BH_4)_3$ may be estimated by summing ionic radii. The effective radii of Zr^{4+} and BH_4^- are respectively 0.89 and 1.6 ± 0.1 Å for the bidentate model with coordination number 9 and 0.98 and 1.36 ± 0.06 Å for the tridentate model with coordination number 12. The expected range of Zr–B distances for a bidentate model is thus 2.39–2.59 Å and for a tridentate one 2.28–2.40 Å. Since our measured values (essentially identical for both models) lie at the overlapping boundary of these regions, the distance criterion for the bridge multiplicity is ambiguous for $(C_5H_5)Zr(BH_4)_3$. There remains only some inferential evidence in the diffraction results that favors the tridentate model: some of the refinement restrictions required to obtain convergence of the bidentate model could be relaxed in the case of the tridentate. One in particular, the amplitude $l(C\cdot B)_{syn}$, we view as important because of the relatively high weight of the $(C\cdot B)_{syn}$ terms.

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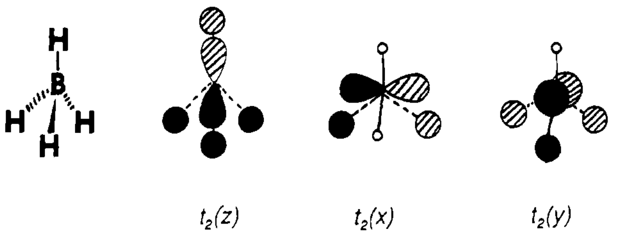

Figure 5. Molecular orbitals of a borohydride moiety.

The Zr–B distance in $(C_5H_5)Zr(BH_4)_3$ is about 0.1 Å longer than that in tetrahedral, tridentate $Zr(BH_4)_4$ (r_a = 2.308 (10) Å[9]), and the Q–Zr–B angle (Q is the centroid of the C_5H_5 ring) is about 6° larger than the tetrahedral value. These differences may be rationalized in terms of steric effects attributable to replacement of a BH_4 group in $Zr(BH_4)_4$ with the bulkier C_5H_5 group. For example, in $(C_5H_5)Zr(BH_4)_3$ repulsions between the C_5H_5 and BH_4 groups and between BH_4 groups are about equal, judged from comparison of the shortest $C{\cdot}BH_4$ distance (~3.4 Å) and the $BH_4{\cdot}BH_4$ distance (~3.8 Å) with the corresponding van der Waals distances (3.6 and 4.0 Å). It may be inferred that these repulsions are similar to those between BH_4 groups in $Zr(BH_4)_4$ because the $BH_4{\cdot}BH_4$ distances in the two molecules are similar. Clearly, both elongation of the Zr–B bond and the bond-angle changes that accompany the substitution of BH_4 with C_5H_5 are consistent with relaxation of the stresses in $(C_5H_5)Zr(BH_4)_3$. These stresses would not be expected to have an important effect on the structure of the C_5H_5 group, and indeed, the C–C bond length and the associated C–C vibrational amplitude are very close to those found for C_5H_5 groups in similar molecules.[22]

The value for Δ(B–H) is smaller than often is found in bridged BH_4 groups, but the associated uncertainties show that little significance can be attributed to the value itself.

EHMO Calculations. The borohydride ligand and its modes of attachment to metals have been the subject of several theoretical studies.[7,29] These are stimulated not only by its own bonding versatility but also as a model for the interaction of methane with metal surfaces. Considering the triply bonded mode, it is clear that suitable donor orbitals are readily generated (i) by interaction of the boron p_z orbital with the in-phase combination of the three hydrogens to produce a σ-type molecular orbital of a_1 symmetry (in C_{3v}) and (ii) from the degenerate pair of boron p_x and p_y orbitals with appropriate hydrogen combinations to generate a π set of e symmetry. To relate these to their original tetrahedral parentage, we designate these as $t_2(z)$, $t_2(x)$, and $t_2(y)$, as shown in Figure 5. It is further apparent that the analogous σ and π donor orbitals of the cyclopentadienide ligand afford a qualitative resemblance; on this basis, it was proposed[5] that there could exist an isolobal relationship[30] between the $(\eta^3\text{-}BH_4)M$ and $(\eta^5\text{-}C_5H_5)M$ moieties. Since the aforementioned electron-diffraction study, together with the infrared and Raman spectroscopic data, supports the viability of the effective replacement of a triply bridged borohydride fragment in $Zr(BH_4)_4$ by a η^5-cyclopentadienyl ligand to give $(\eta^5\text{-}C_5H_5)Zr(\eta^3\text{-}BH_4)_3$, we chose to examine in more detail the frontier orbital interactions between the $[(\eta^3\text{-}BH_4)_3Zr]^+$ moiety and $(\eta^3\text{-}BH_4)^-$ and $(\eta^5\text{-}C_5H_5)^-$ units. Figure 6 shows the results of EHMO calculations on the tris(borohydrido)zirconium cation and reveals that the HOMO is derived entirely from borohydride $t_2(x)$-type combinations. Since the HOMO is of a_2 symmetry, there is no appropriate metal orbital to mix with the ligand combinations. Of more significance for the current problem is the LUMO, which is 87% localized on zirconium and is constructed from 5s, $5p_z$, and $4d_{z^2}$ orbitals; this presents an attractive target for a ligand which can focus its σ donation along the C_3 axis. Slightly above the LUMO lies a degenerate pair of acceptor orbitals that are predominantly of metal d_{xz} and d_{yz} character. Clearly, these latter orbitals are well oriented to interact with pseudocylindrical ligands presenting a filled doubly degenerate π manifold.

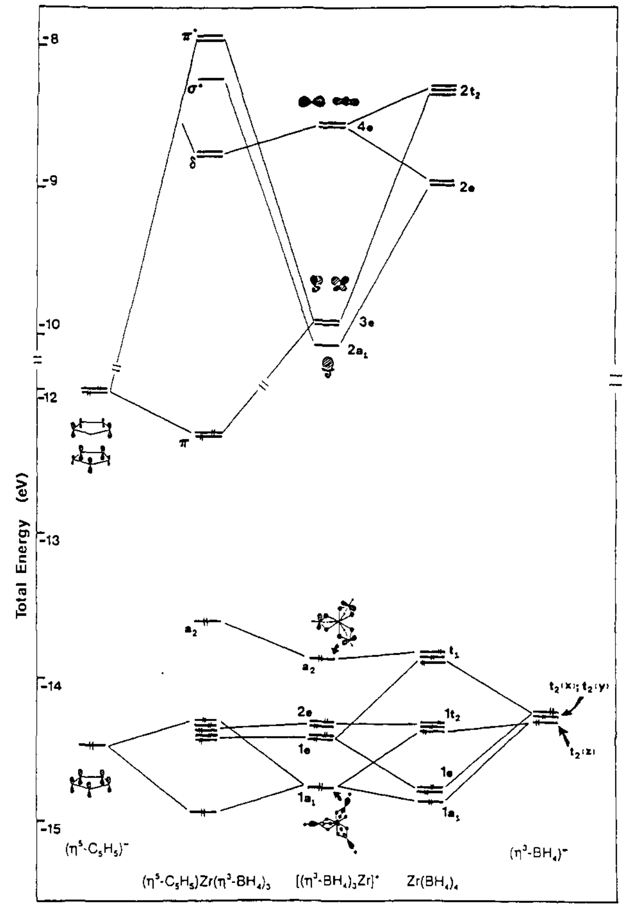

Figure 6. EHMO energy-level diagram showing the interactions of $[Zr(\eta^3\text{-}BH_4)_3]^+$ with borohydride and cyclopentadienide units. (The $1a_1$ and a_2 orbitals of the cation are viewed down the 3-fold axis.)

The HOMO of the $[(\eta^3\text{-}BH_4)_3Zr]^+$ cation and the 2e set below it are almost unaffected by the approach of the fourth borohydride ligand. The strongest interaction involves the 1e set which destabilizes the filled $t_2(x)$ and $t_2(y)$ orbitals of the incoming BH_4^- ligand. These latter orbitals, in combination with the a_2 HOMO of the cation, generate the HOMO of $Zr(BH_4)_4$; this triply degenerate set has t_1 symmetry, thus precluding any contribution from the metal orbitals. The borohydride donor orbitals, viz., $t_2(z)$, $t_2(x)$, and $t_2(y)$, are considerably lower in energy than are the acceptor orbitals of the cation and so the overall stabilization relative to the energy of the separated fragments is only 1.3 eV. In contrast, the HOMO's of the cyclopentadienide ligand, viz., the doubly degenerate π set, provide a much better energy match with the vacant 3e orbitals of $[(\eta^3\text{-}BH_4)_3Zr]^+$ and the observed stabilization on allowing the two fragments to approach and bond is now 2.2 eV. That is, the $C_5H_5^-$ ligand apparently bonds more strongly to the tris(borohydrido)zirconium cation than does a fourth borohydride moiety.

Although the essence of the interaction between $[(\eta^3\text{-}BH_4)_3Zr]^+$ and $(\eta^3\text{-}BH_4)^-$ is relatively straightforward, the correlation diagram appears a little complicated as a result of the high symmetry of the tetrahedral product. Thus, in C_{3v} the d_{xz} and d_{yz} (and also d_{xy} and $d_{x^2-y^2}$) exist as doubly degenerate orbital pairs; these mix in T_d where d_{xz}, d_{yz}, and d_{xy} span the t_2 representation while $d_{x^2-y^2}$ and d_{z^2} make up the e pair. The correlations are perhaps more obvious in $(\eta^5\text{-}C_5H_5)Zr(\eta^3\text{-}BH_4)_3$ where the symmetry decreases from C_{3v} to C_s. In many ways the latter situation parallels the interaction of a $C_5H_5^-$ ligand with the cation $[Mn(CO)_3]^+$, which also possesses three low-lying acceptor orbitals, one of σ and one of π symmetry, although the ordering of the levels is reversed.[31]

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In conclusion, the spectroscopic and electron-diffraction results for $C_5H_5Zr(BH_4)_3$ support the suggestion that direct substitution of a cyclopentadienide ring for one of the borohydride groups in $Zr(BH_4)_4$ does not affect the overall structure much: neither the average B–H bond length nor the B·B distance changes significantly, and although the Zr–B bond lengthens and the B–Zr–B angle decreases, these changes are consistent with the changes in steric effects discussed above.

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Supplementary Material Available: Tables of total intensities and final backgrounds from each plate and average molecular intensities (9 pages). Ordering information is given on any current masthead page.

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Phase Transitions in Cesium 7,8-Dicarbaundecaborate(12): A New One-Dimensional Cesium Solid Electrolyte at 210 °C

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The structural study of the three polymorphs of cesium 7,8-dicarbaundecaborate(12) in the temperature interval 20–250 °C is reported. While the low- and medium-temperature polymorphs (γ and β, respectively) present very poor conductivity, the phase transition to the high-temperature form (α) is associated with an increase of 4 orders of magnitude of the conductivity for Cs^+ ($\sigma = 5.5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$). The structure of the γ-polymorph has been solved by single-crystal X-ray diffraction methods. Crystal data: $Cs[B_9C_2H_{12}]$, monoclinic, space group $P2_1/c$, with $a = 8.360$ (3) Å, $b = 10.696$ (4) Å, $c = 11.222$ (4) Å, $\beta = 92.62$ (2)°, $V = 1002$ Å^3, $Z = 4$, $D_x = 1.75$ g cm^{-3}, μ(Mo Kα) = 36 cm^{-1}, and $F(000) = 496$. The positions of Cs^+ and of the center of mass of the anion in the β-polymorph have been refined by the rigid-body Rietveld refinement technique starting from the corresponding positions in the γ-phase and assuming a $P2_1/c$ space group. Cell parameters at 140 °C: $a = 6.90$ (2) Å, $b = 12.55$ (2) Å, $c = 12.15$ (2) Å, $\beta = 90.0$ (1)°, $V = 1052$ Å^3, $Z = 4$. The crystal structure of the α-polymorph has been deduced from the indexed powder diffraction pattern and corresponds to an I-centered tetragonal cell [$a = 8.64$ (3) Å, $c = 7.14$ (3) Å, $V = 533$ Å^3], with the anions placed at the corners and the center of the cell and the Cs^+ disordered at the $(0, {}^1/_2, {}^1/_4)$ and $(0, {}^1/_2, {}^3/_4)$ sites. The probable conduction path is along the c axis of the tetragonal cell.

Introduction

It is well-known that certain solids, the so-called solid electrolytes, show an abnormally high ionic conductivity. In general, the crystal structure of such compounds consists of one part that remains rigid and of another that is highly disordered at the experimental temperature, i.e. the mobile ions. If we only consider the thermally induced disorder, then two sorts of solid electrolytes can be distinguished depending on the manner of onset of the disorder: those like CaF_2, where the disorder gradually appears with increasing temperature, and the α-AgI type, where the sudden appearance of the disorder is associated with a phase transition. The main factor[1] favoring the easy motion of Ag^+ in α-AgI is, among others, the large number of crystallographic identical jump sites separated by a low potential barrier available for each Ag^+ ion.

In the course of our research on carborane compounds, we have investigated the alkaline-earth-metal series of the nearly spherical $B_9C_2H_{12}^-$ anion. The Cs salt shows a certain parallelism with AgI. First, the ratio of the ionic radii is similar, i.e. $R(Cs^+)/R(B_9C_2H_{12}^-) \cong 1.69/3.43 = 0.49$ and $R(Ag^+)/R(I^-) \cong 1.26/2.16 = 0.58$, and second, the ions are monovalent in both compounds. This parallelism prompted us to further study this compound, specifically the structural characterization and conductivity response. In this paper, we report the conductivity data as a function of the crystallographic form of the compound.

Experimental Section

Synthesis of $B_9C_2H_{12}^-$ and Precipitation of the Cs Salt. The *o*-carborane was partially degraded with KOH in a reaction flask according to Plešek et al.[2] and was precipitated with cesium acetate. The precipitate was filtered out in air and recrystallized from hot water. The subsequent analyses and the spectroscopic results are in agreement with the literature data for this compound. The crystals used in the X-ray diffraction experiments were grown from a solution of the salt in a 1/1 mixture of water and dimethyl formamide.

Table I. Crystallographic Data for γ-$Cs[B_9C_2H_{12}]$ at 26 °C

$a = 8.360$ (3) Å	fw 266.1
$b = 10.696$ (4) Å	space group $P2_1/c$ (No. 14)
$c = 11.222$ (4) Å	cryst dimens 0.20 × 0.12 × 0.15 mm
$\beta = 92.62$ (2)°	$\rho_{calcd} = 1.75$ g cm^{-3}
$V = 1002$ Å^3	$\mu = 36$ cm^{-1}
$Z = 4$	transm coeff 0.77–1.36
$F(000) = 496$	$R(F_o) = 0.052$
$\lambda = 0.71069$ Å	$R_w(F_o) = 0.057$

Electrical Conductivity Measurements. The sample was finely ground, pressed into a cylindrical pellet (6.5 mm in diameter and 4–5 mm thick) under a pressure of 6 atm, and heated in an oven (150 °C) for 2 h but not sintered. Both faces of the sample were coated with evaporated gold, which served as the electrodes. The technique of complex plane impedance analysis was employed to measure the conductivity of the sample in air in the temperature interval 25–350 °C. A Hewlett-Packard impedance analyzer (Model 4192A LF) was used at frequencies ranging between 5 and 13 MHz. The time between consecutive measurements was 20 min.

Differential Scanning Calorimetry. Measurements were done on a DSC2 Perkin-Elmer automated analyzer system in Ar atmosphere (heating rate = 20 K/min).

Crystallography and Structure Determination of $Cs[B_9C_2H_{12}]$ at 26 °C. A colorless fragment of a prismatic crystal was selected for single-crystal X-ray diffraction analysis. Crystal data and relevant structure refinement parameters are given in Table I.

Data were collected on an Enraf-Nonius CAD4 four-circle diffractometer (graphite-monochromatized Mo Kα radiation); 1483 independent reflections with $\theta \leq 25°$ were measured, from which 1176 were observed with $I > 2.5\sigma(I)$. The *hkl* ranges were $-9 \leq h \leq 9$, $0 \leq k \leq 11$, and $0 \leq l \leq 12$. No significant decay of standard reflection intensities

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