CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
OREGON STATE UNIVERSITY, CORVALLIS, OREGON 97331

An Electron-Diffraction Investigation of Zirconium Tetraborohydride, $Zr(BH_4)_4$[1]

BY VERNON PLATO AND KENNETH HEDBERG*

Received June 10, 1970

The results of an electron-diffraction investigation of $Zr(BH_4)_4$ vapor are in agreement with predictions based upon a tetrahedral arrangement of the heavy atoms with three bridging hydrogen atoms between each boron atom and the zirconium atom. The bond distance (r_a), bond angle, and root-mean-square vibrational amplitude (l_a) values are $r(\text{Zr–B}) = 2.308$ (0.010) Å, $r(\text{Zr–H}_b) = 2.21$ (0.04) Å, $r(\text{B–H}_t) = 1.18$ (0.12) Å, $r(\text{B–H}_b) = 1.27$ (0.05) Å, $\angle \text{H}_b\text{BH}_b = 108.4$ (2.1)°, $l(\text{Zr–B}) = 0.045$ (0.010) Å, $l(\text{Zr–H}_b) = 0.139$ (0.055) Å, $l(\text{B–H}_t) = 0.07$ (0.12) Å, and $l(\text{B–H}_b) = 0.072$ (0.044) Å; parenthesized values are 2σ and include estimates of correlation and systematic error. The BH_4 groups are probably undergoing torsional motion of considerable amplitude about the Zr–B bond vector. The bond distances are shown to correspond to a total bond number in good agreement with the number of bonding electrons.

Introduction

A steady accumulation of structural evidence during the past few years has made it clear that hydrogen bridge bonds play an important role in the metal borohydrides. This has been especially well documented for covalent compounds of the lighter metals, for example $Al(BH_4)_3$[2] and $Be(BH_4)_2$[3] (although the geometry of the latter is not yet known with certainty), and for the boron hydrides[4] themselves. For the heavior metal compounds the evidence is equally compelling but less extensive: infrared and nmr data for $Zr(BH_4)_4$ and $Hf(BH_4)_4$[5] indicate the presence of hydrogen bridges, as do the results of an X-ray diffraction investigation of the former.[6]

The structure of $Zr(BH_4)_4$ in the crystal is interesting. The molecule was found to have T_d symmetry (assuming no disorder) with a single terminal B–H bond collinear with each Zr–B vector, thus implying *three* hydrogen bridges for each Zr $\cdots$ B pair (Figure 1). The bridging atoms themselves were not located with certainty. The T_d symmetry for the molecule in the crystal at −160° contrasts with the D_{4d} or D_{4h} symmetry suggested for the gaseous molecule by the infrared work. Although it seemed unlikely that the structure of the gas-phase molecule differed in any essential way from that in the crystal, we felt that an electron-diffraction study of the vapor was important. In addition to settling the symmetry question the structural results could be expected to include more accurate intramolecular distance values than were obtained in the X-ray work.

During the final stages of our work the results of Spiridonov and Mamawa's (hereafter referred to as SM) electron-diffraction investigation appeared.[7] Because our results are more complete (they include measurements of vibrational amplitudes) and differ from SM's in some important details, we felt their presentation to be worthwhile.

Experimental Section

The sample of $Zr(BH_4)_4$ was prepared and purified by Dr. R. Walsh of this university; its purity was estimated at >99%. The sample bulb was fitted with a Teflon stopcock and the joint by which the bulb was connected to the stainless steel nozzle of the diffraction apparatus was lubricated with a Teflon grease. Before each series of exposures the bulb was evacuated at liquid N_2 temperatures in order to remove any hydrogen gas resulting from possible sample decomposition.

Electron-diffraction photographs were made in the new Oregon State apparatus[8] using Kodak process plates, an r^3 sector, nozzle-to-plate distances of 75 and 30 cm, electron-beam currents of 0.1–0.2 μA, and an accelerating voltage of 44 kV. The electron wavelength was calibrated against CO_2 gas[9] in separate experiments.

Two plates from the longer and three from the shorter camera distance were selected for analysis. These were handled essentially in the way previously described[10] to yield five individual $sI(s)$ curves which were then combined[10] to give a single composite intensity curve with data over the range $1.75 \leq s \leq 31.75$ in intervals $\Delta s = 0.25$.

Structure Analysis

Trial Structure.—The composite intensity curve from the procedure described above was in the "variable-coefficient" form

$$sI_m(s) = \sum_{i,j}{}' n_{ij}A_iA_jr_{ij}^{-1}V_{ij} \cos |\eta_i - \eta_j| \sin r_{ij}s \quad (1)$$

where $s = 4\pi\lambda^{-1} \sin \theta$ (2θ is the scattering angle), n_{ij} is the multiplicity of the interatomic distance r_{ij}, A_i is a modified electron scattering amplitude, V_{ij} is a molecular vibration factor, and η_i is a phase factor. The curve is shown in Figure 2. Radial distribution curves were calculated from the "constant coefficient"

---

(1) Supported by the National Science Foundation under Grant GP-8453.

(2) See A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **22**, 328 (1968), and references cited therein.

(3) See T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, **91**, 774 (1969), and references cited therein.

(4) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, Chapter 1.

(5) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *J. Chem. Soc. A*, 182 (1966).

(6) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967).

(7) V. P. Spiridonov and G. I. Mamawa, *J. Struct. Chem.*, **10**, 120 (1969).

(8) A description of this apparatus will be published elsewhere.

(9) The distance standards were $r_a(\text{CO}) = 1.1642$ Å and $r_a(\text{O}\cdots\text{O}) = 2.3244$ Å obtained from $r_a \approx r_e + \delta r + \langle\Delta r\rangle - \langle\Delta r^2\rangle/r_e$ with $r_e = 1.1600$ Å (C. P. Courtoy, *Can. J. Phys.*, **35**, 608 (1957)), $\delta r = 0.0002$ Å (calculated by the method described earlier: M. Iwasaki and K. Hedberg, *J. Chem. Phys.*, **36**, 2961 (1962)), and $\langle\Delta r\rangle = 0.00503$ Å and $\langle\Delta r^2\rangle = 0.00121$ Å (K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **40**, 505 (1967)).

(10) G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1969). One of the plates made at the long distance was unevenly exposed due to a slight beam deflection induced by an electrostatic charge buildup during exposure and could not be rotated during densitometry. Instead, data from ten scans along slightly different diametrical lines were averaged to give a single data set.

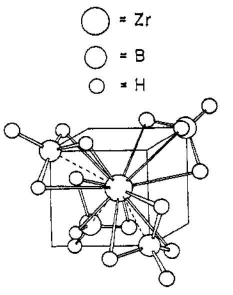

Figure 1.—Diagram of the $Zr(BH_4)_4$ structure.

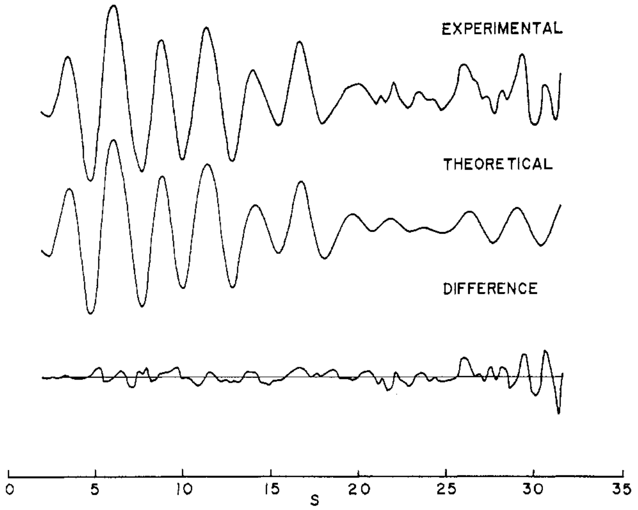

Figure 2.—Intensity curves. The experimental curve is a composite of data from two camera distances. The theoretical curve corresponds to the final results. The difference curve is the experimental minus the theoretical.

curve $I_m'(s) = Z_{Zr}Z_B(A_{Zr}A_B)^{-1}sI_m(s)$ according to

$$D(r) = \sum_{s_{min}}^{s_{max}} I_m'(s) \exp(-Bs^2) \sin rs\Delta s \qquad (2)$$

using A's derived[10] from tabulated[11] values of the electron-scattering amplitudes and, later, intensity data in the unobserved range $0 \leq s \leq 1.50$ from theoretical curves corresponding to good models. One such curve is shown in Figure 3. (See Table I for intensity data of $Zr(BH_4)_4$.)

The experimental radial distribution curves showed a peak at 1.2 Å which is due to the bridge and terminal B–H bonds, a stronger peak at 2.3 Å due to the Zr–B and Zr–H bridge bonds, and a combination of rather weak, unresolved peaks extending over the range 2.7–5.3 Å arising from the nonbonding distances. The B···B distance was not immediately apparent with certainty, but the plausible assignment to it of the strongest component of the constellation of weak peaks gave a calculated B–Zr–B angle close to the tetrahedral value (2 arc sin (3.75/(2)(2.30)) = 109°). Since the curve had no peak of any substance at 3.25 Å, which would correspond to a 90° bond angle, we tentatively assigned the molecule a tetrahedral heavy-atom structure rather than a square-coplanar one. Subsequent calculation of theoretical radial distribution curves verified this assignment. There remained the important questions of the number of bridge bonds and the orientation of the BH_4 groups about the Zr–B bond vector. Trial models with three hydrogen bridge bonds were found which gave theoretical radial distribution curves in good agreement with the observed curve. However, no two-bridge model in even rough agreement with the indications of the experimental curve in the $r > 3.0$ Å region could be found. This difference in quality of the two types of models is illustrated by the curves of Figure 3. No other types of models seemed

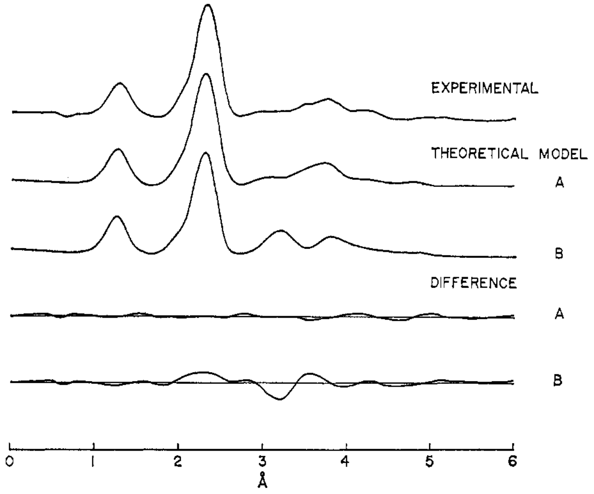

Figure 3.—Radial distribution curves. The theoretical curves correspond (A) to the final results for the three-bridge model and (B) to one of the best two-bridge models found. B = 0.0024.

TABLE I

INTENSITY DATA FOR ZIRCONIUM TETRABOROHYDRIDE[a]

s \ Δs	0.00	0.25	0.50	0.75
2.00	-288	-373	-373	-245
3.00	129	633	957	849
4.00	333	-568	-1464	-1915
5.00	-1597	-716	133	1194
6.00	1888	2119	1933	1202
7.00	59	-934	-1339	-1716
8.00	-1283	-781	225	1093
9.00	1307	962	232	-686
10.00	-1405	-1368	-847	-171
11.00	507	1067	1541	1513
12.00	1052	283	-553	-1320
13.00	-1480	-1210	-576	107
14.00	440	599	357	152
15.00	-213	-410	-627	-652
16.00	-329	187	716	1174
17.00	1223	845	300	-140
18.00	-587	-643	-517	-321
19.00	-253	-48	157	208
20.00	233	265	158	48
21.00	-92	-231	-2	-181
22.00	-76	288	-10	-163
23.00	-333	-263	-24	50
24.00	-85	-156	-122	-247
25.00	-387	-258	-141	13
26.00	529	659	562	307
27.00	528	-130	-71	-126
28.00	-474	-78	59	-162
29.00	105	400	858	641
30.00	-422	-738	-627	154
31.00	87	-227	-636	432

[a] The data are in the form corresponding to eq 1 of the text; *i.e.*, corrections arising from calibration of the sector and from nonlinear response of the photographic emulsion to the scattered electron intensity have been applied and the background has been subtracted.

---

(11) H. L. Cox, Jr., and R. A. Bonham, *J. Chem. Phys.*, **47**, 2599 (1967).

worthy of consideration, and accordingly we gave our attention to investigation of the parameters of the three-bridge model. Approximate values for this model as derived from the analyses of radial distribution curves were Zr–B = 2.3_0 Å, Zr–H_b = 2.2_0 Å, B–H_b = 1.2_5 Å, B–H_t = 1.1_8 Å, and $\angle H_bBH_b = 109°$; the orientation of the BH_4 groups about the Zr–B bond vector appeared to be such as to stagger the bridging hydrogen atoms with the three distant Zr–B bonds.

Structure Refinement.—Refinement of the structure was carried out by least squares based on intensity curves[12] defined by eq 1 using the experimental composite curve described earlier and shown in Figure 2. Three-bridge models[13] of symmetry T were defined in terms of the following five geometrical parameters: the average of the Zr–B and Zr–H_b distances ($\langle$Zr–B,$H_b\rangle$), the difference between these distances (Δ(Zr–B,H_b) = r(Zr–B) − r(Zr–H_b)), the average and difference of the two types of B–H distances ($\langle$B–H$\rangle$ and Δ(B–H) = r(B–H_b) − r(B–H_t)), and the torsional angle of the BH_4 groups (ϕ). Refinable vibrational parameters were taken to be the root-mean-square amplitudes (l) associated with the Zr–B, Zr–H_b, Zr···H_t, B–H_b, B–H_t, and B···B distances.

Of the above geometrical parameters the torsional angle was clearly the weakest. Instead of attempting to refine it directly, we decided to carry out a series of refinements based on trial models differing from each other only in the values (held constant) assigned this angle. Although such torsionally static models are hardly realistic, the relatively very weak B···H and longer H···H scattering which comprises the information about the torsion angle suggested that refinements of more sophisticated models would have little meaning; comparison of radial distribution curves calculated for torsionally static and torsionally active models confirmed this conclusion. The best results for the torsionally static model were obtained with $\phi = 38°$, where $\phi = 0°$ corresponded to the eclipsed conformation of the bridges and Zr–B bonds. Distances and vibrational amplitudes for this model are given in Table II and the corresponding theoretical intensity and radial distribution curves are shown in Figures 2 and 3, respectively.

TABLE II

DISTANCES AND AMPLITUDES OF VIBRATION[a] FOR THE MODEL WITH A 38° TORSION ANGLE

Type	r_a, Å	σ_{LS}[a]	l_a, Å	σ_{LS}[b]
		Torsion Insensitive		
Zr–B	2.308	0.003	0.045	0.003
Zr–H_b	2.211	0.014	0.139	0.019
B–H_t	1.176	0.042	0.067	0.040
B–H_b	1.272	0.018	0.072	0.016
Zr···H_t	3.485	0.041	0.176	0.072
B···B	3.770	0.005	0.105	0.014
B···H_t	4.779	0.037	(0.120)	
H_b···H_b	2.064	0.028	(0.120)	
H_t···H_t	5.690	0.068	(0.120)	
H_b···H_t	2.012	0.026	(0.120)	
		Torsion Sensitive		
B···H	3.000		(0.120)	
B···H	3.516		(0.120)	
B···H	4.230		(0.120)	
H···H	1.958		(0.120)	
H···H	2.446		(0.120)	
H···H	2.525		(0.120)	
H···H	2.850		(0.120)	
H···H	3.137		(0.120)	
H···H	3.565		(0.120)	
H···H	3.700		(0.120)	
H···H	3.744		(0.120)	
H···H	3.802		(0.120)	
H···H	3.897		(0.120)	
H···H	4.070		(0.120)	
H···H	4.317		(0.120)	
H···H	4.409		(0.120)	
H···H	4.502		(0.120)	
H···H	4.502		(0.120)	

[a] Parenthesized values were assumed. [b] Standard deviations from least squares do not include estimates of systematic error.

Final Results.—The results of the least-squares calculations showed that the values derived for the bond distances, the distances reflecting only one bond angle, and their associated amplitudes were essentially independent of the torsion angle ϕ. The torsion-insensitive distances and amplitudes of Table II thus represent fairly the parameters of the $Zr(BH_4)_4$ structure regardless of the best value for ϕ. Because ϕ is a parameter which does not express the surely complicated torsional motions taking place, we are not inclined to weight very heavily the value of 38° found to give the best agreement with experiment. However, this value does lead to torsion-dependent B···H distances which plausibly account for three of the more obvious features of the long-distance part of the radial distribution curve, features which can hardly be imagined to find explanation in any possible distribution of H···H distances.[14] We interpret the 38° result as the approximate value of an average torsion angle.

Our final results are summarized in Table III. The errors have been calculated from the formulas

$$2\sigma_r = 2(2\sigma_{LS}^2 + (0.0005r)^2)^{1/2} \tag{3}$$

$$2\sigma_l = 2(2\sigma_{LS}^2 + (0.02l)^2)^{1/2} \tag{4}$$

$$2\sigma_\angle = 2\sqrt{2}\sigma_{LS} \tag{5}$$

where σ_{LS} was obtained from the least-squares process, the factor 2 takes into account possible correlation among the observations, and the terms involving r and l are estimates of possible systematic error.[15] Our usual practice of reporting 2σ values as errors appears to lead to especially conservative statements of the values of some of the weaker parameters, such as the distances and amplitudes for the pairs B–H_t and Zr···H_t. The uncertainty in the location of the terminal hydrogen atoms implied by these results is very likely due to the small weight of the B–H_t and Zr···H_t scattering com-

---

(12) K. Hedberg and M. Iwasaki, *Acta Crystallogr.*, **17**, 529 (1964).

(13) Two-bridge models were also briefly examined. The results led to no essentially better fit than was obtained from the radial distribution curve analysis and this type of model was given no further attention.

(14) The distribution of H···H distances shown in Table I is actually one of the simplest. If ϕ is taken to be different for each of the BH_4 groups, there arise four times as many distances. In all cases these distances are essentially smoothly distributed over a range of about 2 Å.

(15) K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, **36**, 589 (1962).

TABLE III

FINAL RESULTS[a] FOR $Zr(BH_4)_4$

	Parameter				
	This work				SM[b]
	r_a	2σ	l_a	2σ	r_a
Zr–B	2.308	0.010	0.045	0.010	2.35 ± 0.01
$Zr–H_b$	2.211	0.04	0.139	0.055	2.10 ± 0.02
$B–H_t$	1.18	0.12	0.07	0.12	
					1.19 ± 0.01
$B–H_b$	1.272	0.05	0.072	0.044	
$Zr\cdots H_t$	3.48	0.12	0.18	0.20	
$B\cdots B$	3.770	0.016	0.10	0.04	
$\angle H_bBH_b$	108.4	2.1			
ϕ	38[c]				

[a] Distances and amplitudes in Ångströms; angles in degrees. [b] Reference 7. [c] Angle of torsion of BH_4 groups giving best agreement; see text.

bined with strong vibration effects (such as shrinkage) effecting the latter.

The theoretical intensity and radial distribution curves corresponding to the final results are shown in Figures 2 and 3, respectively. The correlation matrix[12] is given in Table IV.

TABLE IV

CORRELATION MATRIX CORRESPONDING TO FINAL RESULTS FOR $Zr(BH_4)_4$[a]

k[b]	l(Zr–B)	$l(Zr–H_b)$	$l(B–H_t)$	$l(B–H_b)$	$l(Zr–H_t)$	$l(B\cdots B)$	r(Zr–B)	$r(Zr–H_b)$	$r(B–H_t)$	$r(B–H_b)$	$r(Zr\cdots H_t)$	$r(B\cdots B)$	$\angle H_bBH_b$
1.000	0.550	0.701	0.175	0.256	0.211	0.192	−0.250	−0.468	0.100	−0.792	0.081	−0.250	−0.364
	1.000	0.321	0.057	0.128	0.085	0.108	−0.115	−0.105	0.027	−0.016	0.018	−0.115	−0.071
		1.000	0.105	0.213	0.181	0.158	−0.582	−0.254	0.136	−0.020	0.091	−0.582	−0.122
			1.000	0.788	−0.083	−0.078	−0.138	−0.015	0.706	−0.909	0.701	−0.138	0.239
				1.000	−0.041	−0.048	−0.164	−0.062	0.746	−0.746	0.883	−0.164	0.160
					1.000	0.420	−0.094	−0.220	−0.658	0.116	−0.070	−0.094	−0.213
						1.000	−0.077	−0.127	−0.077	0.107	−0.083	−0.077	−0.129
							1.000	−0.135	−0.141	0.117	−0.063	0.999	−0.033
								1.000	0.007	−0.042	−0.004	−0.135	0.946
									1.000	−0.691	0.997	−0.141	0.021
										1.000	−0.687	0.117	−0.310
											1.000	−0.063	0.180
												1.000	−0.333
													1.000

[a] The standard deviations to be used with this table are the σ_{LS} of Table II. [b] Amplitude scale constant.

Discussion

The results of our investigation of $Zr(BH_4)_4$ are in agreement with the three-bridge configuration suggested by the low-temperature X-ray work and the previous gas-phase electron-diffraction study. However, there are some important differences (Table III) in the values of the bond distances obtained in the two electron-diffraction studies which deserve comment.

Our results for the Zr–B and $Zr–H_b$ bond lengths are, respectively, 0.04 Å shorter and 0.10 Å longer than those reported by SM and the differences might appear to be significant. We believe, however, that they are more illusory than real and are the consequence of quite different approaches to the problem of deduction of the structure.[16] The two types of distances themselves differ by only 0.10–0.15 Å and, as has been noted, are not resolved in the radial distribution curve. Such situations are commonly found to yield a rather large range of models, characterized by essentially the same *average* distance but different distance splits and different associated amplitudes of vibration, which give approximately the same quality of fit to the observations. That such may be the case here is strongly indicated by the fact that the weighted average of SM's Zr–B and $Zr–H_b$ distances at 2.243 Å lies close to ours at 2.266 Å.

There exists another, more substantial disagreement concerning the nature of the B–H bonds and their lengths. SM interpret their results in terms of four equivalent B–H bonds, whereas our results can only be satisfactorily interpreted in terms of two types of B–H bonds. Further, the quantitative disagreement between our average B–H distance of 1.248 Å and SM's of 1.19 ± 0.01 Å is more serious than at first might be thought, for although the errors associated with each component of this average are large in the present work, these errors arise almost entirely from σ_{LS} and thus are correlated. From Table IV the correlation coefficient connecting them is seen to be negative so that the values of the $B–H_b$ and $B–H_t$ distances, taking into account error, tend to move in opposite directions. Indeed, an error of +0.10 Å in $r(B–H_t)$ leads to a predicted error of $-0.687(0.018/0.041)(0.10) = -0.03$ Å in $r(B–H_b)$ and thus to only a very small change in the weighted-average B–H distance (from 1.248 to 1.250 Å). While SM's B–H bond length is not implausible for terminal B–H links as judged from results on other compounds, a similar, forced interpretation of our data in terms of only terminal-type B–H bonds would lead to an unreasonably large value for the bond length and the vibrational amplitude, and generally poorer agreement between theoretical and experimental intensities. Largely for this reason we are inclined to believe our results for the B–H bonds are the more accurate.[17]

---

(16) Our least-squares procedure led to the simultaneous refinement of four geometrical and six vibrational parameters. Although SM tested several possible *configurations* for the molecule, it is not clear from their report that a systematic study of the geometrical parameters of the tetrahedral model was carried out. There is no mention of any investigation of vibration parameters.

(17) There is also a puzzling discrepancy between SM's experimental radial distribution curve and the theoretical curve presumably calculated for their model which adds weight to our conclusion: the B–H bond peak in the experimental curve lies at an obviously larger distance than does the corresponding theoretical peak.

Insofar as we are aware the structure of $Zr(BH_4)_4$ is unique in having three hydrogen bridge bonds linking each boron atom to the metal atom; otherwise the structure does not appear to be unusual. A tetrahedral arrangement of ligands around zirconium atoms has been observed in $ZrCl_4$,[18] for example, and the structure of the BH_4 groups is similar to that found in $Al(BH_4)_3$[2] ($B\text{-}H_t = 1.196 \pm 0.012$ Å, $B\text{-}H_b = 1.283 \pm 0.012$ Å, $\angle H_bBH_b = 114.2 \pm 0.2°$).

The bonds involving the zirconium atom are all considerably longer than the sum of the covalent radii corrected for electronegativity difference.[19] Thus, if one uses the value 1.36 Å for the zirconium radius, deduced from $r(\text{Zr–Cl}) = 2.32$ Å in $ZrCl_4$ with the aid of the formula[20] $r(\text{A–B}) = r_A + r_B - 0.02|\chi_A - \chi_B|$, then the lengths of the Zr–B and Zr–H bonds predicted from the same formula (but with the constant 0.02 replaced with 0.08[21]) are, respectively, 2.12 and 1.61 Å. Somewhat better agreement is obtained using Pauling's metallic radii,[21] which without the electronegativity correction yield the values 2.25 and 1.76 Å. At first glance these long distances appear to have no explanation in terms of simple valence-bond concepts except a qualitative one: each of the four zirconium bonding electrons is involved in bonding to three hydrogen atoms and a boron atom with the result that on the average a one-quarter bond is formed with each. However, a somewhat more satisfying picture of the bonding may be developed using a method applied by one of us[22] to the hydroborons and their derivatives. In the case of $Zr(BH_4)_4$, as with these molecules, the ligancy of the heavier atoms exceeds the number of bonding orbitals suggesting bonding situations (from the valence-bond point of view) similar to those encountered in metals and intermetallic compounds. One might expect that Pauling's empirical equation[20] $D(n) = D(1) - 0.600 \log n$, where $D(n)$ and $D(1)$ are interatomic distances for a bond of fractional bond number and a single bond, could be applied. If one takes $D(1)$ equal to 2.20, 1.76, and 1.16 Å for Zr–B, Zr–H, and B–H, respectively, calculated from Zr, B, and H radii of 1.45, 0.80, and 0.37 Å using the electronegativity correction, these bonds in $Zr(BH_4)$ are calculated to have bond numbers of 0.66, 0.18, 0.66 ($B\text{-}H_b$) and 0.93 ($B\text{-}H_t$). The weighted sum of these is 16.44 corresponding to 32.88 bonding electrons, which is to be compared with the number 32 available from the outer shells of the atoms. The agreement is especially good in view of the sensitivity of the calculation: a decrease of only 0.01 Å in the radius of the hydrogen atom, for example, leads to 31.6 calculated bonding electrons.

Acknowledgment.—We wish to thank the National Science Foundation for financial support. We are indebted to Dr. R. Walsh for preparation of the sample.

(18) V. Spiridonov, P. A. Akishin, and V. I. Tsirel'nikov, *J. Struct. Chem.* **3**, 311 (1962).

(19) V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 37 (1941).

(20) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, Chapter 7.

(21) Reference 20, Chapter 11.

(22) K. Hedberg, *J. Amer. Chem. Soc.*, **74**, 3486 (1952).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

Synthesis and Reactions of Novel Bridged Dicarbollide Complexes Having Electron-Deficient Carbon Atoms

BY JAMES N. FRANCIS AND M. FREDERICK HAWTHORNE*[1]

Received August 4, 1970

Reaction of the bis-π-dicarbollide ligand complexes of Co^{3+} and Fe^{3+} with CS_2 in the presence of $AlCl_3$ and HCl produced the first examples of zwitterionic species having an $\text{-S-C}^+\text{H-S-}$ bridge between boron atoms of the two dicarbollide ion ligands of the complex. Similarly, a suspected $\text{-OC}^+(CH_3)\text{O-}$ bridged species results from the reaction of acetic acid–acetic anhydride with an $HClO_4$ catalyst. Further transformations of these species are described.

In a previous communication[2] we have briefly reported the structure and synthesis of the compound shown in Figure 1 in conjuction with Churchill and Gold. It was obtained by an acid-catalyzed addition of carbon disulfide to $(1,2\text{-}B_9C_2H_{11})_2Co^-$ with concomitant evolution of hydrogen gas (eq 1). Similar reactions (eq 2, 3) with a variety of ligands have been previously observed[3] with the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions but not with any metallocarborane complexes. We

$$(1,2\text{-}B_9C_2H_{11})_2Co^- + CS_2 + H^+ \longrightarrow (1,2\text{-}B_9C_2H_{10})_2CoS_2CH + H_2 \quad (1)$$

$$B_{10}H_{10}^{2-} + L + H^+ \longrightarrow B_{10}H_9L^- + H_2 \quad (2)$$

---

(1) To whom correspondence should be addressed at the Department of Chemistry, University of California, Los Angeles, Calif. 90024.

(2) M. R. Churchill, K. Gold, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1222 (1969).

(3) (a) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, **4**, 280 (1965); (b) W. R. Hertler and M. S. Raasch, *J. Amer. Chem. Soc.*, **86**, 3661 (1964); (c) W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *ibid.*, **86**, 3973 (1964); (d) W. H. Knoth, J. C. Sauer, J. H. Balthis, H. C. Miller, and E. L. Muetterties, *ibid.*, **89**, 4842 (1967); (e) M. D. Marshall, R. M. Hunt, G. T. Hefferan, R. M. Adams, and J. M. Makhlouf, *ibid.*, **89**, 3361 (1967).