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Synthesis and X-ray and Neutron Structures of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$

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The complex Zr(9-BBN)$_4$ [9-BBN = $(\mu\text{-}H)_2BC_8H_{14}$] has been synthesized via the reaction of K(9-BBN) with $ZrCl_4$ in diethyl ether. The structure of the title compound has been determined by X-ray and neutron single-crystal diffraction techniques. Each 9-BBN ligand is coordinated to the Zr atom via two B–H–Zr bridges, and these metal–ligand bonding interactions are further augmented by three prominent C–H···Zr agostic interactions. Average molecular parameters derived from the neutron analysis: Zr–H = 2.051(8) Å, B–H = 1.286(7) Å, Zr···B = 2.409(6) Å, Zr–H–B = 87.7(4)°, H–Zr–H = 58.9(3)°. The Zr···H distances corresponding to the three C–H···Zr agostic interactions are 2.424(7), 2.663(8), and 2.551(7) Å. The fourth potential C–H···Zr interaction has a Zr···H distance [3.146(7) Å] that is too long to be considered in the agostic range. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffraction system, and neutron diffraction data were collected on the quasi-Laue diffractometer VIVALDI at the Institut Laue-Langevin; the final agreement factor for the neutron analysis is 6.52% for 2557 reflections with $I > 2\sigma(I)$.

Introduction

Coordination complexes containing the simplest hydroborate anion BH_4^- as a ligand have received considerable attention for quite some time.[1−3] These molecules are of interest because they may serve as reducing agents or precursors for the synthesis of molecules with bridging or terminal hydrides or other inorganic materials such as borides.[2f,g] They could also serve as catalysts for certain organic reactions.[2a]

The first structure of a d^0 tetrahydroborate complex, $Zr\{(\mu\text{-}H)_3BH\}_4$ (Chart 1), was determined by an X-ray diffraction study at −160 °C in 1967[3d] and by an electron diffraction investigation of the same molecule in the gas phase in 1971.[3c] Those structural determinations were in substantial agreement with each other: the molecule was found to have essentially tetrahedral symmetry with a single terminal B−H bond collinear with each Zr···B vector and the remaining three hydrogens at bridging positions between

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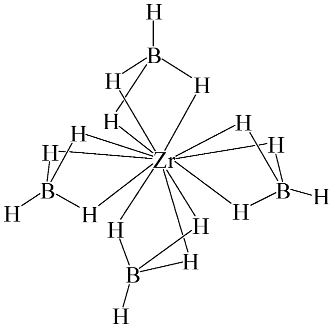
Chart 1



the zirconium and boron atoms. This basic structure was subsequently confirmed by a single-crystal neutron diffraction study on the analogous hafnium complex, $Hf\{(\mu\text{-}H)_3BH)\}_4$, in 1983.[4]

Some of us[5] have reported the preparation and chemistry of organohydroborate derivatives that contain, in addition, the cyclopentadiene (Cp) ligand: (a) $Cp_2MX\{(\mu\text{-}H)_2BR_2\}$ [M = Zr, Hf; X = Cl, H, D, CH_3, CH_2Ph, $OSiPh_3$; BR_2 = BC_4H_8, BC_5H_{10}, BC_8H_{14}], (b) $Cp_2M\{(\mu\text{-}H)_2BR_2\}$ [M = Ti, Nb; R_2 = C_4H_8, C_5H_{10}, C_8H_{14}], (c) $CpZr\{(\mu\text{-}H)_2BR_2\}_3$ [BR_2 = BC_5H_{10}, BC_8H_{14}], (d) $CpZrCl\{(\mu\text{-}H)_2BC_8H_{14}\}_2$. We have also reported a few other organohydroborate derivatives that do not contain the Cp ligand.[6] In the present paper, we describe the preparation and characterization of a new 9-BBN hydroborate complex of zirconium as well as the X-ray and neutron diffraction analyses of its structure. $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ is the first example of an organohydroborate derivative from group 4 without Cp. Unlike the $M[(\mu\text{-}H)_3BH]_4$ (M = Zr, Hf) complexes, all of the B−H groups in this compound are involved in bridging interactions to the metal atom. Interestingly, three agostic interactions were formed between the α C−H of three BC_8H_{14} units and zirconium metal in this molecule. Agostic interactions are of general consequence in organometallic chemistry since they often lead to C−H activation and may serve to stabilize various catalytic species.[7−9]

Experimental Section

General Procedures. All manipulations were carried out on a standard high vacuum line or in a drybox under a nitrogen atmosphere. Diethyl ether and hexane were distilled under nitrogen from Na/benzophenone. All solvents for vacuum line manipulations were stored in a vacuum over a Na/K alloy. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were vacuum transferred from the Na/K alloy. $ZrCl_4$ and $(C_8H_{14})B(\mu\text{-}H)_2(BC_8H_{14})$ (9-BBN dimer) were purchased from Aldrich and used as received. Potassium hydride (35 wt % dispersion in mineral oil) was purchased from Aldrich, washed with hexane, and dried under vacuum prior to use. $K(H_2BC_8H_{14})$[10] was prepared by literature procedures. NMR spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 250.11 MHz at 303 K, and boron 11 spectra were externally referenced to BF_3OEt_2 (δ 0.00). Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer with 2 cm^{-1} resolution.

Preparation of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$. A solution of $K(H_2BC_8H_{14})$ (324.2 mg, 2.0 mmol) in 50 mL of diethyl ether was added dropwise to a solution of $ZrCl_4$ (116.5 mg, 0.5 mmol) in 100 mL of diethyl ether. After the mixture was stirred at room temperature for 12 h, the white solid (KCl) was removed by filtration, and after the solvent was removed under vacuum, a white product was obtained. This white solid was redissolved in ether and kept at −30 °C for crystallization. White crystalline $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ was obtained in a 78% yield. ^{11}B NMR (ether): δ 17.47. ^1H NMR (methylene chloride-d_2): δ 1.96−1.85 (m, β-H), 1.76−1.67 (m, β-H and γ-H), 1.60 (br s, μ-H), 1.56−1.52 (m, s, α-H). IR (KBr): 2979 (m), 2947 (m), 2918 (s), 2899 (s), 2873 (s), 2833 (s), 2654 (w), 1967 (m), 1923 (m), 1446 (m), 1387 (s), 1341 (s), 1284 (m), 1203 (m), 1111 (m), 923 (m), 829 (m). Anal. Calcd for $C_{32}H_{64}B_4Zr$: C, 65.89; H, 11.06. Found: C, 66.12; H, 11.08.

X-ray Structural Determination. Single-crystal X-ray diffraction data were collected using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius Kappa CCD diffraction system. A single crystal of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ was mounted on the tip of a glass fiber coated with Fomblin oil (a pentafluoropolyether), and crystallographic data were collected at 150 K. Unit cell parameters were obtained by indexing the peaks from the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polariza-

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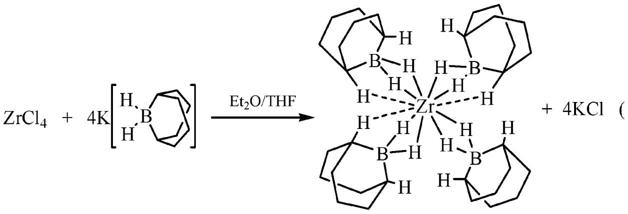
tion effects using the Denzo-SMN package (Nonius BV, 1999).[11] An absorption correction was applied using the SORTAV program[12] provided by MaXus software.[13] The structure was solved by direct methods and refined using SHELXTL-97[14] (difference electron density calculation, full matrix least-squares refinements). All non-hydrogen atoms were located and refined anisotropically.

Neutron Structure Determination. Crystals of the title compound are stable at room temperature but are extremely air-sensitive. A suitable "neutron-sized" crystal with approximate dimensions of 0.9 × 0.9 × 0.9 mm^3 was mounted in a 2 mm diameter quartz capillary, wedged between two plugs of quartz wool, inside an argon-filled glovebox. The crystal was cooled to 150 K, and data were collected on the Very-Intense Vertical-Axis Laue Diffractometer (VIVALDI) at the Institut Laue-Langevin.[15] Eleven Laue diffraction patterns, each accumulated over 4 h, were collected at (mostly) 20° intervals in a rotation of the crystal perpendicular to the incident beam. A total of 14 032 reflections were recorded of which 4642 were independent, corresponding to 64% of the complete unique set to $d = 0.78$ Å, the average minimum value of d observed over all patterns. The intensities were indexed and processed using the program LAUEGEN,[16a,b] and the reflections were integrated and the background was removed using the program INTEGRATE+.[16c] The reflections were normalized to a constant incident wavelength using the program LAUENORM.[16d] This normalization would also have corrected for the absorption variation in this nearly spherical sample. Subsequent calculations for structure determination were carried out using the SHELXTL package.[14] Initial H positions were obtained from the results of the earlier X-ray structure determination. Least-squares refinement of all atomic coordinates and anisotropic temperature factors resulted in a final agreement factor of $R(F) = 6.52\%$ for 2557 independent reflections with $I > 2\sigma(I)$. Relevant crystallographic data are summarized in Table 1. Since only the ratios between unit cell dimensions can be determined in the white-beam Laue technique, the dimensions found by X-ray diffraction were used in the neutron refinement; the observed ratios and angles were, however, in accord with the X-ray values.

Results and Discussion

Synthesis and Characterization. The complex $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ was obtained in 78% yield from the reaction of $ZrCl_4$ and 4 mol of $K(H_2BC_8H_{14})$ in diethyl ether or THF (reaction 1)



(1)

Table 1. Crystallographic Data for $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$

	X-ray Analysis	
empirical formula	$C_{32}H_{64}B_4Zr$	
fw	583.29	
cryst syst, space group	triclinic, $P\bar{1}$	
unit cell dimensions	$a = 11.246(2)$ Å	$\alpha = 92.65(2)°$
	$b = 11.388(2)$ Å	$\beta = 96.55(2)°$
	$c = 12.898(2)$ Å	$\gamma = 91.80(2)°$
V	1638.46(2) Å^3	
Z, calcd density	2, 1.182 g/cm^3	
temperature	150 (2) K	
cryst size	0.40 × 0.31 × 0.23 mm^3	
absorption coefficient	0.355 mm^{-1}	
wavelength	0.71073 Å	
GOF	1.181	
no. of reflns collected	7509	
no. of independent reflns	7509	
no. of reflns with $I > 2\sigma(I)$	6691	
R1 [$I > 2\sigma(I)$]	0.0292	
wR2 (all data)	0.0971	
	Neutron Analysis[a]	
temperature	150(1) K	
wavelength range of reflns accepted	0.9−2.7 Å	
cryst size	0.9 × 0.9 × 0.9 mm^3	
min d spacing observed	0.72 Å	
θ range for data collcn	4−72°	
no. of reflns collected	14032	
no. of independent reflns	4642	
no. of reflns with $I > 2\sigma(I)$	2557	
no. of params refined	860	
refinement method	full matrix, least-squares on F^2	
GOF[b]	1.137	
final R indices [$I > 2\sigma(I)$]	R1 = 0.0652, wR2 = 0.0985	
R indices (all data)	R1 = 0.1637, wR2 = 0.1130	

[a] Unit cell parameters for the neutron analysis (and their estimated standard deviations) were assumed to be the same as those for the X-ray analysis since both data sets were collected at the same temperature. [b] With $w = 1/[\sigma^2(F_o{}^2) + (0.03P)^2]$, where $P = [\max(F_o{}^2, 0) + 2F_c{}^2]/3$

This complex is composed of four 9-BBN hydroborate ligands, each functioning as a bidentate ligand. The white solid complex is stable at room temperature in the absence of air, and it is soluble in THF and diethyl ether as well as benzene. In diethyl ether, it slowly decomposes to the 9-BBN dimer, $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$, and an unknown material. Upon decomposition of the title zirconium/9-BBN hydroborate complex, the color of the ether solution becomes dark (from colorless to yellow to brown), a process which can be monitored in solution by ^{11}B NMR spectroscopy at room temperature. Initially, only one resonance (17.47 ppm), that of the pure complex of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$, was present in the spectrum. After two days, the signal at 17.47 ppm had noticeably diminished and two new peaks became observable: one at 27.28 ppm corresponding to the 9-BBN hydroborate dimer $[(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})]$ and another unidentified signal at 15.50 ppm. After two weeks at room

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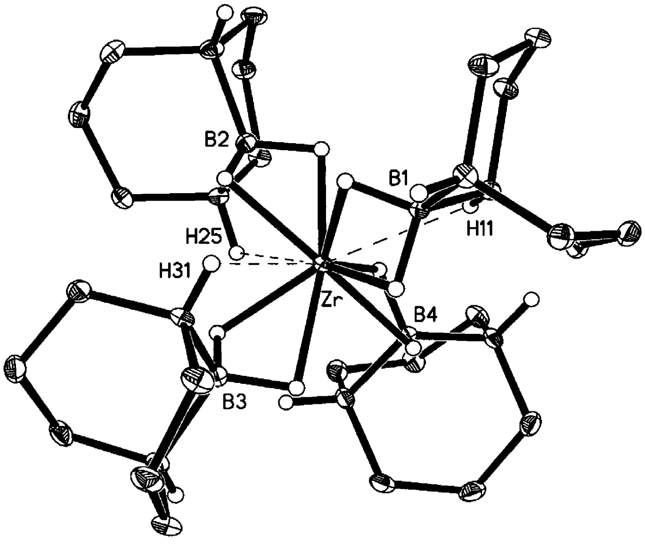

Figure 1. Molecular structure of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ from the X-ray analysis; the ellipsoids are shown at 50% probability.

temperature, the original signal at 17.47 ppm had completely disappeared indicating that the complex $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ had completely decomposed to the 9-BBN hydroborate dimer $[(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})]$ and an unknown material in diethyl ether. Unfortunately, we could not isolate and characterize the latter species. In the ^1H NMR spectrum of the title compound, $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$, the hydrogen signals of the 9-BBN hydroborate ligand appeared at $\delta = 1.96-1.84$, $1.76-1.66$, and $1.56-1.52$ ppm, consistent with those in the complex $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$.[5c] The signals at 1.60 ppm are assigned to the bridging hydrogen atoms. We attempted to abstract a hydride ion from $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ by employing $B(C_6F_5)_3$ in toluene and in diethyl ether, but the product was too unstable to be isolated. The initial ^{11}B NMR spectrum at room temperature consists of a doublet at -24.68 ppm in toluene and -23.98 ppm in ether which indicates the formation of an anion with a B−H bond. However, this signal disappeared very quickly at room temperature. A ^{13}C NMR spectrum was also obtained, but the proximity of the boron atom made agostic interactions nonobservable.

Solid-state infrared spectra of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ show that most of the C−H stretches occur in the normal region from 2979 to 2833 cm^{-1}. However, weak absorption also appeared at a lower frequency, 2655 cm^{-1}, which might be evidence of agostic M−H−C interactions in this molecule.[7b] Bands assigned to M−H−B stretches appear from 1967 to 1923 cm^{-1} in this compound.

X-ray Structural Results. The solid-state structure of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ was initially determined by a single-crystal X-ray diffraction analysis (Figure 1). Crystallographic data and selected bond distances and angles are given in Tables 1 and 2.

Suitable single crystals of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ were obtained by crystallization from diethyl ether at −30 °C. Each of the four 9-BBN hydroborate units functions as a bidentate ligand bonded to the zirconium atom through two hydrogen bridges. Unlike the arrangement of hydroborate ligands in

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Zr(9-BBN)$_4$

Bond Lengths

	X-ray	neutron
Zr···B(1)	2.352(2)	2.344(5)
Zr···B(2)	2.421(2)	2.412(7)
Zr···B(3)	2.388(2)	2.383(6)
Zr···B(4)	2.501(2)	2.496(5)
average	2.416(2)	2.409(6)
Zr−H(1A)	2.01(2)	2.036(9)
Zr−H(1B)	1.94(2)	2.016(7)
Zr−H(2A)	1.98(2)	2.084(7)
Zr−H(2B)	1.92(2)	2.061(9)
Zr−H(3A)	2.01(2)	2.107(9)
Zr−H(3B)	1.95(2)	2.035(7)
Zr−H(4A)	2.01(2)	2.052(7)
Zr−H(4B)	1.95(2)	2.014(9)
average	1.971(13)	2.051(8)
B(1)−H(1A)	1.19(2)	1.295(8)
B(1)−H(1B)	1.16(2)	1.303(7)
B(2)−H(2A)	1.22(2)	1.269(15)
B(2)−H(2B)	1.19(2)	1.284(7)
B(3)−H(3A)	1.18(2)	1.302(7)
B(3)−H(3B)	1.11(2)	1.248(15)
B(4)−H(4A)	1.20(2)	1.301(10)
B(4)−H(4B)	1.16(2)	1.286(9)
average	1.18(2)	1.286(7)
Zr···H(11)	2.449(21)	2.424(7)
Zr···H(25)	2.663(22)	2.663(8)
Zr···H(31)	2.579(25)	2.551(7)
Zr···H(45)	3.222(23)	3.146(7)
C(11)−H(11)	0.953(22)	1.124(9)
C(25)−H(25)	0.976(23)	1.119(9)
C(31)−H(31)	0.874(26)	1.131(8)
C(45)−H(45)	1.013(24)	1.111(8)

Bond Angles

	X-ray	neutron
B(1)−Zr−B(2)	106.73(7)	106.6(2)
B(1)−Zr−B(3)	114.06(7)	114.4(2)
B(1)−Zr−B(4)	111.50(7)	111.5(2)
B(2)−Zr−B(3)	110.24(7)	109.9(2)
B(2)−Zr−B(4)	112.45(7)	112.8(2)
B(3)−Zr−B(4)	101.98(7)	101.9(2)
average	109.9(7)	109.5(2)
H(1A)−Zr−H(1B)	52.4(9)	59.4(3)
H(2A)−Zr−H(2B)	52.2(9)	58.3(3)
H(3A)−Zr−H(3B)	50.2(9)	58.0(4)
H(4A)−Zr−H(4B)	52.9(8)	59.9(3)
average	51.9(9)	58.9(3)
Zr−H(1A)−B(1)	90.7(11)	86.4(5)
Zr−H(1B)−B(1)	94.2(11)	87.1(3)
Zr−H(2A)−B(2)	95.0(11)	88.5(4)
Zr−H(2B)−B(2)	99.9(11)	89.1(5)
Zr−H(3A)−B(3)	94.3(13)	85.2(5)
Zr−H(3B)−B(3)	96.6(13)	89.7(4)
average	95.1(13)	87.7(4)
Zr−H(4A)−B(4)	97.5(6)	93.5(5)
Zr−H(4B)−B(4)	102.6(7)	95.8(5)
Zr···B(1)−C(11)	86.51(11)	86.9(2)
Zr···B(2)−C(25)	92.99(11)	93.2(3)
Zr···B(3)−C(31)	86.52(10)	89.7(2)
Zr···B(4)−C(45)	107.29(12)	107.4(2)
B(1)−C(11)−H(11)	118.0(13)	118.2(4)
C(12)−C(11)−H(11)	104.8(13)	104.4(4)
C(18)−C(11)−H(11)	105.5(13)	104.6(5)
B(2)−C(25)−H(25)	115.8(13)	116.5(5)
C(24)−C(25)−H(25)	105.8(13)	105.3(5)
C(26)−C(25)−H(25)	106.3(13)	105.2(4)
B(3)−C(31)−H(31)	117.7(17)	117.5(5)
C(32)−C(31)−H(31)	106.2(17)	105.2(5)
C(38)−C(31)−H(31)	104.1(16)	104.4(5)
B(4)−C(45)−H(45)	119.2(13)	115.0(4)
C44−C45−H45	102.5(13)	107.6(5)
C46−C45−H45	106.1(13)	105.3(6)

Zr{(μ-H)$_2$BH}$_4$, [3c,3d] a symmetrical tetrahedral configuration, the four boron atoms that surround Zr in the title compound are in a slightly distorted tetrahedral arrangement [B···Zr···B angles = 114.06(7)°, 106.73(7)°, 110.24(7)°, 111.50(7)°, 101.98(7)°, 112.45(7)°]. The Zr···B distances in this complex are also slightly unequal [2.352(2), 2.388(2), 2.421(2), 2.501(2) Å] but are still comparable to the Zr···B distance of 2.34(3) Å in Zr(BH$_4$)$_4$.[3c,3d] In contrast, the Zr···B distances in the complex CpZr{(μ-H)$_2$BC$_8$H$_{14}$}$_3$ are significantly longer [2.541(2), 2.544(2), 2.556(2) Å].[5c] The average Zr-bridge−hydrogen bond length in the title compound is 1.97 Å, similar to those in two other known complexes, CpZr(Cl){(μ-H)$_2$BC$_8$H$_{14}$}$_2$ (1.98 Å)[5c] and Cp*Zr(Cl){(μ-H)$_2$BC$_8$H$_{14}$}$_2$ (1.99 Å).[5c] In the complex reported here, Zr{(μ-H)$_2$BC$_8$H$_{14}$)}$_4$, zirconium is formally associated with 16 valence electrons, but interestingly, the "electron deficiency" of zirconium appears to be partially compensated by three agostic interactions involving the α C−H bonds of three of the BC$_8$H$_{14}$ units, Zr···H11 = 2.449(21) Å, Zr···H25 = 2.663(22) Å, Zr···H31 = 2.579(25) Å. These estimated distances were later measured more accurately by the subsequent neutron diffraction analysis (vide infra). All three Zr···H distances are less than the sum of the zirconium covalent radius and the hydrogen van der Waals radius, 2.70 Å (Zr,[17] 1.50 Å; H,[18] 1.20 Å). Because of these agostic interactions, three of the Zr···B−C angles are highly distorted [Zr···B(1)−C(11) = 86.51(11)°, Zr···B(2)−C(25) = 92.99(11)°, Zr···B(3)−C(31) = 89.40(10)°] as compared to the fourth angle [Zr···B(4)−C(45) = 107.29(12)°] whose BBN ligand has a much weaker agostic interaction with the zirconium atom. This might be the first example of three dominant agostic interactions between hydrogen and metal in one molecule. If these agostic interactions are included, 22 electrons are associated with zirconium. In contrast, in the case of zirconium tetrahydroborate, Zr[(μ-H)$_3$BH)]$_4$, there are 24 electrons associated with zirconium.[1c,3c,d]

Neutron Structural Results. Essentially, the results from the earlier X-ray analysis were confirmed, but the neutron analysis provided more precise H atom parameters. Notably, the neutron-determined B−H bond lengths are longer, as expected, and more nearly equal. As anticipated, each BBN ligand was found to coordinate to the metal atom in a bidentate fashion. It was mentioned earlier that the overall geometry of the title complex (especially the Zr···B−C angles) is severely strained due to the presence of agostic interactions from three of the BBN ligands. Analysis of the neutron data resulted in a more accurate characterization of these three agostic bond distances [Zr···H11 = 2.424(7) Å, Zr···H25 = 2.663(8) Å, Zr···H31 = 2.551(7) Å] which are in good agreement with the values calculated from the X-ray data. As a result of these interactions, the compound displays a pronounced tilting of the three agostically related BBN ligands relative to the metal center as revealed by the average Zr···B−C angle of 89.9(2)° (involving Zr···B1−C11, Zr···B2−C25, and Zr···B3−C31) as opposed to the opposite Zr···B−C angle average of 161.2(3)° (involving Zr···B1−C15, Zr···B2−C21, and Zr···B3−C35). In fact, the fourth BBN ligand may show evidence of being weakly agostic as demonstrated by the inequality of the two Zr···B−C angles associated with it [107.4(2)° and 143.5(2)°]. However, the associated Zr···H45 bond distance of 3.146(7) Å involving the fourth BBN ligand is noticeably longer than the other three interactions and does not support the notion of a fourth agostic interaction. The average bond distance of the three α C−H bonds that interact with Zr (C11−H11, C25−H25, and C31−H31) is 1.125(9) Å, which is very slightly longer than the average bond distance of the other five α C−H bonds with no or very weak interaction with Zr metal [1.109(8) Å]. A summary of selected bond distances and angles from the neutron study is given in Table 2.

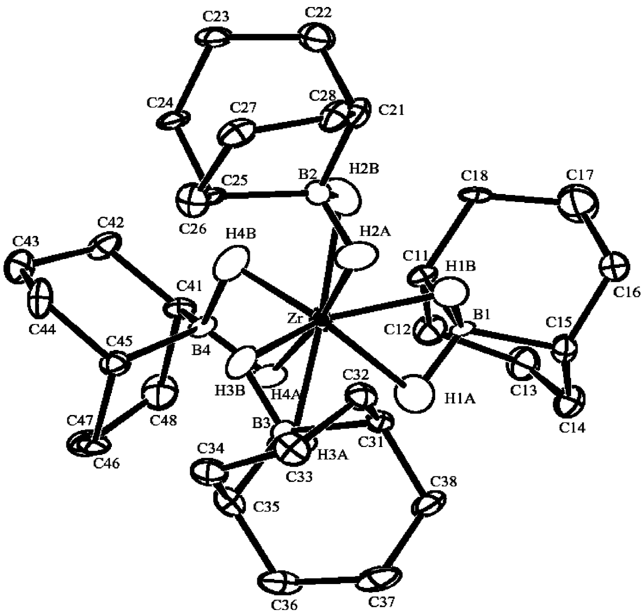

Figure 2. Neutron structure of Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_4$ showing the eight hydride positions with 50% probability ellipsoids.

Our neutron data analysis has provided the first accurate neutron-diffraction measurement of a Zr−H−B bridge bond. The Zr−hydride distances range from a minimum of 2.014(9) Å to a maximum of 2.107(9) Å, giving an average Zr−H distance of 2.051(8) Å. Other average molecular parameters are as follows: B−H = 1.286(7) Å, Zr···B = 2.409(6) Å, Zr−H−B = 87.7(4)°, and H−Zr−H = 58.9(3)°. One other feature worth mentioning is that this complex demonstrates a slight distortion in the bidentate bridges: the strained character arising from the bicyclic framework of the BBN ligand is apparent in the low H−Zr−H "bite angle" [average = 58.9(3)°]. In addition, the Zr−H−B angles [average Zr−H−B = 87.7(4)°] are much smaller for the three agostically related BBN ligands than that for the fourth ligand (with boron atom B4) where no interaction is apparent [average Zr−H−B = 94.7(5)°].

Neutron studies of other group IV metal−hydride−boron complexes that involve bidentate ligands have been reported. In an earlier paper on Hf(BH$_4$)$_2$(η^5-CH$_3$C$_5$H$_4$)$_2$,[19] the average

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(17) Howard, W. A.; Tina, M. T.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900.

(18) Huheey, J.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, 1993; Table 8.1, p 292.

(19) Johnson, P. L.; Cohen, S. A.; Marks, T. J.; Williams, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2709

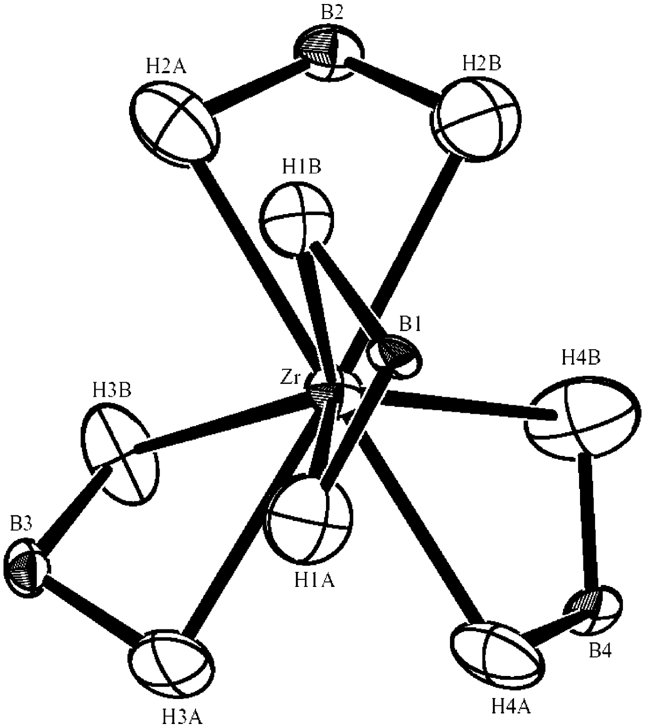

Figure 3. ORTEP plot of the core structure of Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_4$ derived from neutron data, showing the Zr−hydride−boron bridge bonds. The carbon atoms and the hydrogen atoms of the C−H bonds have been removed for clarity. Atoms are shown as 50% probability ellipsoids.

Hf−H distance was reported to be 2.095(8) Å. In a very recent paper we published containing a Ti−H−B bridge,[5e] the average Ti−H distance was found to be 1.919(16) Å. The Zr−H distances from the present work [average = 2.051(3) Å] are significantly longer than the average Ti−H distance but slightly shorter than the Hf−H distance which is in keeping with the expected trend in covalent radii of Ti < Zr < Hf. Furthermore, the Zr−H−B bridge bond angles [average = 87.7(4)°] are consistently smaller, except for the agostic free BBN ligand, compared to the other group IV complexes that have been analyzed by neutron diffraction [average for Ti−H−B = 95.4(12)°, average for Hf−H−B = 96.8(7)°]. However, strictly speaking, a comparison between the M−H−B angles of the three compounds may not really be meaningful as a consequence of the strain of the BBN ligands in the present work. Figures 2−4 show ORTEP plots of the neutron structure of Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_4$.

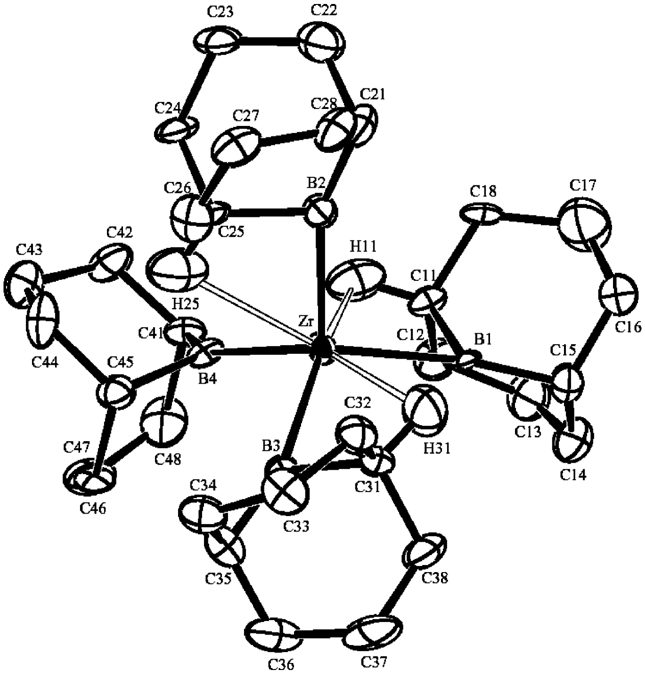

Figure 4. ORTEP plot of the neutron structure of Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_4$ with 50% probability ellipsoids showing the three major agostic interactions. All H atoms in the molecule except those involved in the agostic interactions have been removed for clarity. Note highly distorted geometry caused by these agostic interactions (e.g., compare the Zr−B2−C21 and Zr−B2−C25 angles).

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Supporting Information Available: X-ray and neutron crystallographic files for structural analysis of the title compound Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_4$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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