Preparation and crystal structures of an ionic triple-hydrogen-bridged derivative of 9-BBN hydroborate zirconium(IV)

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Abstract

An ionic dinuclear triple-hydrogen-bridged 9-BBN hydroborate zirconium complex, $[K(Et_2O)_4][\{(\mu\text{-}H)_2BC_8H_{14}\}_3Zr(\mu\text{-}H)_3Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_3]$ (**1**) was formed from the reaction of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ with KH and aniline in diethyl ether. The molecular structure of compound **1** was determined by single-crystal X-ray diffraction analysis. Six 9-BBN hydroborate ligands are coordinated to two Zr atoms via two bridging H atoms, and two Zr atoms are connected by three bridging hydrogens in the anion part of this molecule. The distance of Zr···Zr is 3.1025(5) Å. The crystal structure of **1** suggests that agostic interactions between the zirconium metal center and α-C–H of the 9-BBN hydroborate ligand exist in the solid state. The Zr···H distances corresponding to the α-C–H···Zr *agostic* interactions are 2.579(4) Å and 2.743(4) Å.
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Keywords: Zirconium; B–H–B bridges; 9-BBN hydroborate; Crystal structures; Agostic interactions

1. Introduction

Organometallic complexes containing transition metal-hydride bonds have attracted a great deal of attention [1], due to the challenges of synthesis and characterization, the remarkable range of bonding types and a variety of stoichiometric transformations and catalytic processes. Transition metal-hydrides are believed to be the active species or intermediates in many traditional reactions, such as olefin polymerization, hydrogenation, and hydroformylation. Almost all of the major industrial catalytic processes in the petrochemical industry employ transition metal-hydride species [1b].

Group 4 metal-hydrides play an important role in organic reactions. One of the most important examples is zirconocene hydrochloride ($Cp_2Zr(H)Cl$). This complex was first prepared by Wailes from Cp_2ZrCl_2 and $LiAlH_4$ in 1970 [2]. Subsequent studies of Schwartz and Hart [3] showed that this hydride reacts with a variety of olefins to form isolable alkylzirconium(IV) complexes, $Cp_2Zr(R)Cl$, under mild conditions (see Scheme 1), and the chemistry of zirconocene hydrochloride developed rapidly [4,5]. Today, the complex $Cp_2Zr(H)Cl$ is a very popular organic synthesis reagent. It is generally referred to as "Schwartz's reagent" because of the pioneering studies of Schwartz and his group.

Many studies of zirconocene hydrides syntheses focus on the replacement of a cyclopentadienyl ligand ($C_5H_5^-$) by an alkyl cyclopentadienyl ligand ($C_5H_4R^-$) to produce a more soluble complex to increase the rate of the overall process [6]. Comparatively, synthesis and chemistry of non-cyclopentadienyl group 4 metal hydride complexes, especially polyhydrides, are little known [7]. Girolami and co-workers reported the synthesis and structure of some dinuclear and trinuclear zirconium and hafnium polyhydrides in the early 1990s [7f,7g]. Treatment of the zirconium and hafnium tetrahydroborate, $M(BH_4)_4$ with trimethylphosphine at room temperature produced $M_2H_3(BH_4)_5(PMe_3)_2$ and $M_3H_6(BH_4)_6(PMe_3)_4$. Reactions with 1,2-bis(dimethylphosphino)ethane (dmpe) produced $M_2H_4(BH_4)_4(dmpe)_2$, $MH_2(BH_4)_2(dmpe)_2$, and

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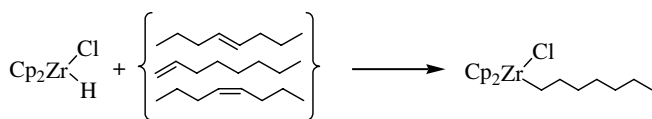
Scheme 1.
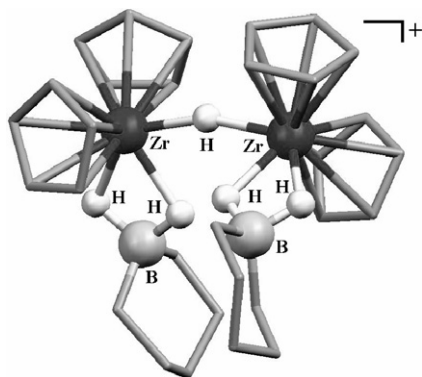
Fig. 1. The structure of $[(\mu\text{-H})\{Cp_2Zr(\mu\text{-H})_2BC_4H_8\}_2]^+$.

$MH(BH_4)_3(dmpe)$. Later, Fryzuk and co-workers [7c,7d] reported that the side on bound dinitrogen complex, $[(^iPr_2PCH_2SiMe_2)_2N]Zr(\mu\text{-}\eta^2\text{-}N_2)[(^iPr_2PCH_2SiMe_2)_2N]$ reacted with dihydrogen to produce a very interesting complex including both bridge N_2 and bridge H_2, $[(^iPr_2PCH_2SiMe_2)_2N]Zr(\mu\text{-}\eta^2\text{-}N_2)(\mu\text{-}\eta^2\text{-}H_2)[(^iPr_2PCH_2SiMe_2)_2N]$.

In this laboratory, we prepared the first example of an unsupported bimetallic hydrogen-bridged cation species, $[(\mu\text{-H})\{Cp_2Zr(\mu\text{-H})_2BC_4H_8\}_2]^+$ [8] (Fig. 1), from the reaction of $Cp_2ZrH\{(\mu\text{-H})_2BC_4H_8\}$ with $B(C_6F_5)_3$ in benzene. More recently, we reported a 9-BBN hydroborane complex of zirconium [9], $Zr\{(\mu\text{-H})_2BC_8H_{14}\}_4$, Both X-ray and neutron diffraction analyses show three *agostic* interactions between the α-C–H of three BC_8H_{14} units and zirconium metal in this molecule. In our continuing studies of organohydroborate zirconium complexes, we studied the reaction of $Zr\{(\mu\text{-H})_2BC_8H_{14}\}_4$ with aniline. The product was impure and crystals of sufficient quality for X-ray examination could not be obtained. However, with KH added to the system an ionic triple-hydrogen-bridged Zr(IV) dinuclear complex, $[K(Et_2O)_4][\{(\mu\text{-H})_2BC_8H_{14}\}_3Zr(\mu\text{-H})_3Zr\{(\mu\text{-H})_2BC_8H_{14}\}_3]$ was produced. In this complex, α-C–H hydrogens on the BC_8H_{14} unit of the 9-BBN hydroborate ligand form *agostic* interactions with the central zirconium atoms in the solid state. We describe here the preparation and structure of this compound.

2. Experimental

2.1. General data

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 vacuum over Na/K alloy. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were vacuum transferred from the Na/K alloy prior to use. $ZrCl_4$ 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 and was washed with hexane and dried under vacuum prior to use. $Zr\{(\mu\text{-H})_2(BC_8H_{14})\}_4$ [9] and $K(H_2BC_8H_{14})$ [10] were prepared by the literature procedures. NMR spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 250.11 at 303 K and Boron-11 spectra were externally referenced to BF_3OEt_2 ($\delta = 0.00$ ppm). Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer with 2 cm^{-1} resolution.

2.2. Preparation of $[K(Et_2O)_4][\{(\mu\text{-H})_2BC_8H_{14}\}_3Zr(\mu\text{-H})_3Zr\{(\mu\text{-H})_2BC_8H_{14}\}_3]$

$Zr\{(\mu\text{-H})_2(BC_8H_{14})\}_4$ (583.4 mg, 1.0 mmol) was placed in a 100 mL flask and dissolved in 50 mL of diethyl ether in a drybox. KH (20.1 mg, 0.5 mmol) and aniline (93.0 mg, 1.0 mmol in diethyl ether) were added to the solution. The mixture was stirred at room temperature for 12 h, then filtered through Celite. The solution was concentrated and stored at $-30\,°C$ to give complex $[K(Et_2O)_4][\{(\mu\text{-H})_2BC_8H_{14}\}_3Zr(\mu\text{-H})_3Zr\{(\mu\text{-H})_2BC_8H_{14}\}_3]$ as white needles in 28% yield. ^{11}B NMR (toluene-d_8): $\delta = 16.16$ ppm. ^{1}H NMR (toluene-d_8): $\delta = 3.57$ (s, μ-H of Zr–H–Zr), 1.96–1.81 (m, β-H), 1.68–1.64 (m, β-H and γ-H), 1.60 (br,s, μ-H of B–H–Zr), 1.51–1.45 (m, s, α-H) ppm. IR(KBr): 2979 (m), 2915 (s), 2876 (s), 2836 (s), 2655 (w), 1942 (s) Anal. Calc. for $C_{56}H_{119}B_6O_4Zr_2K$: C, 58.84; H, 10.49. Found: C, 59.33; H, 11.08%.

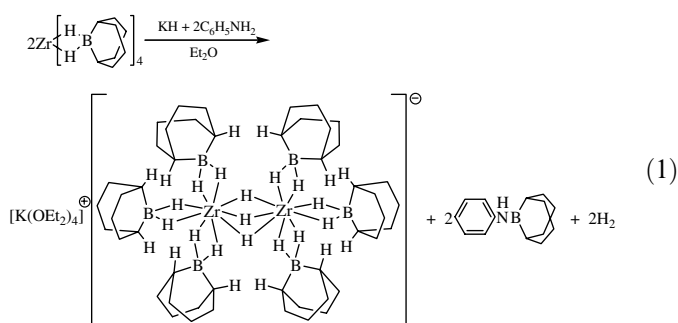### 2.3. X-ray structural determination

Single-crystal X-ray diffraction data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius Kappa CCD diffraction system. A single crystal of $[K(Et_2O)_4][\{(\mu\text{-H})_2BC_8H_{14}\}_3Zr(\mu\text{-H})_3Zr\{(\mu\text{-H})_2BC_8H_{14}\}_3]$ 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 polarization 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 the SHELXTL-97 [14] (difference electron density calculation, full-matrix least-squares refinements). All non-hydrogen atoms were located and refined anisotropically.

3. Results and discussion

3.1. Synthesis and characterization

Complex $[K(Et_2O)_4][\{(\mu\text{-}H)_2BC_8H_{14}\}_3Zr(\mu\text{-}H)_3Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_3]$ (**1**) was obtained in 28% yield from the reaction of $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ with KH and aniline in diethyl ether (Reaction (1)). It is a white solid, and is stable at room temperature in the absence of air. It is soluble in common organic solvents, such as benzene, toluene, diethyl ether, and THF, but slowly decomposes. Some $[(C_5H_{10}B)\text{-}(\mu\text{-}H)]_2$, BBN hydroborane dimer, can always be detected

$$2Zr\left[\begin{array}{c}H\\\cdot B\cdot\\H\end{array}\right]_4 \xrightarrow[\text{Et}_2\text{O}]{\text{KH} + 2\text{C}_6\text{H}_5\text{NH}_2}$$

$$[K(OEt_2)_4]^{\oplus} \left[\text{structure} \right]^{\ominus} + 2 \text{ (aniline-BBN)} + 2H_2 \quad (1)$$

from ^{11}B NMR in the solution of complex **1**.

In the ^1H NMR spectrum of compound **1** in toluene-d_8, proton signals of the 9-BBN hydroborane ligand appeared at $\delta = 1.96\text{–}1.81$, $1.68\text{–}1.64$, and $1.51\text{–}1.45$ ppm, consistent with those in the complexes $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$ and $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_3$ [15]. The signals at 1.60 ppm are assigned to the B–H–Zr bridging hydrogen atoms, and the signals at 3.57 ppm are assigned to the Zr–H–Zr bridging hydrogen atoms, consistent with those reported for $Zr_3H_6(BH_4)_6(PMe_3)_4$ [7f]. We did not find clear NMR information related to *agostic* M–H–C interactions.

Solid state infrared spectra of $[K(Et_2O)_4][\{(\mu\text{-}H)_2BC_8H_{14}\}_3Zr(\mu\text{-}H)_3Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_3]$ show that most C–H stretches occur in the normal region, from 2979 cm^{-1} to 2836 cm^{-1}. However, a weak absorption is present at a lower frequency, 2655 cm^{-1}, consistent with the presence of *agostic* M–H–C interactions in this molecule (see Section 3.2). Bands assigned to M–H–B stretches appear around 1942 cm^{-1} in this compound.

3.2. X-ray structural results

The solid state structure of $[K(Et_2O)_4][\{(\mu\text{-}H)_2BC_8H_{14}\}_3Zr(\mu\text{-}H)_3Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_3]$ was determined by a single-crystal X-ray diffraction analysis. Crystallographic data are given in Table 1, and molecular structures are shown in Fig. 2, while selected bond distances and angles are reported in Table 2.

Table 1
Crystallographic data for $[K(Et_2O)_4][\{(\mu\text{-}H)_2BC_8H_{14}\}_3Zr(\mu\text{-}H)_3Zr\{(\mu\text{-}H)_2BC_8\text{-}H_{14}\}_3]$

|	
Formula	$KC_{64}H_{139}B_6O_4Zr_2$
Formula weight	1259.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	15.7587(2)
b (Å)	21.0412(3)
c (Å)	22.1759(3)
α (°)	
β (°)	91.745(1)
γ (°)	
V (Å^3)	7349.72(17)
Z	4
D_{calc} (g cm^{-3})	1.138
T (K)	150(2)
Crystal size (mm)	$0.3 \times 0.12 \times 1.10$
Number of reflections collected	11 505
Number of reflections with $[I > 2\sigma(I)]$	7981
Absorption coefficient (mm^{-1})	0.380
Final R indices $[I > 2\sigma(I)]$ data	$R_1 = 0.0482$, $wR_2 = 0.0956$
R indices (all data)	$R_1 = 0.0854$, $wR_2 = 0.1108$
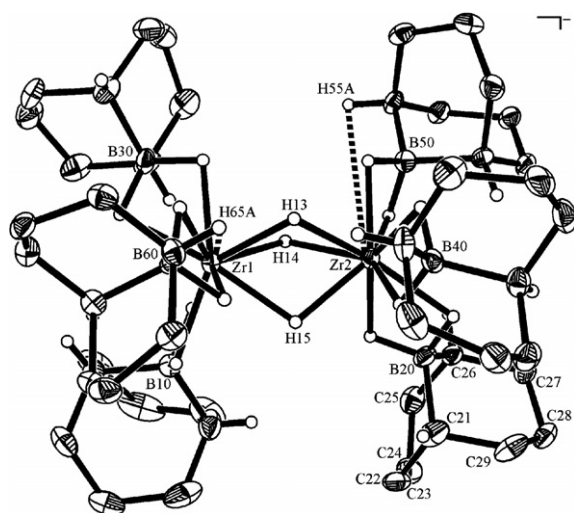
Fig. 2. Molecular structure of $[\{(\mu\text{-}H)_2BC_8H_{14}\}_3Zr(\mu\text{-}H)_3Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_3]^-$.

Suitable single crystals of $[K(Et_2O)_4][\{(\mu\text{-}H)_2BC_8H_{14}\}_3Zr(\mu\text{-}H)_3Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_3]$ (**1**), were obtained by crystallization from diethyl ether at -30 °C. The molecular structure of the anion part of **1** is shown in Fig. 2. In this dinuclear anion, each zirconium metal atom is bonded by three 9-BBN hydroborate units through two hydrogen bridges as a bidentate ligand. Two $[\{(\mu\text{-}H)_2BC_8H_{14}\}_3Zr]$ units are bridged by three, three-centered-two-electron Zr–H–Zr bonds. The distance of Zr···Zr (3.1025(5) Å) is slightly longer than the sum of the zirconium covalent radii (3.0 Å) [16], and comparable to those of $[Li(THF)_2(Cl)\text{-}Li(THF)_2][\{Zr(L)\}_2(\mu\text{-}H)_3]^-$ (L = 2,6-bis (4-*tert*-butyl-6-methylsalicy)-4-*tert*-butylphenol) (3.1630(10) Å) [7a], $Zr_2H(\mu\text{-}H)_3(BH_4)_4(dmpe)_2$ (3.150(1) Å) [7f], $Zr_2(\mu\text{-}H)_3(BH_4)_5(PMe_3)_2$ (3.124(1) Å) [7g], $(C_5Me_5)_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (3.126(1) Å) [17]. The Zr···Zr distance in **1** is

Table 2
Bond lengths (Å) and angles (°) for [K(Et$_2$O)$_4$][{(μ-H)$_2$BC$_8$H$_{14}$}$_3$Zr(μ-H)$_3$-Zr-{(μ-H)$_2$BC$_8$H$_{14}$}$_3$]

Zr(1)–B(10)	2.586(5)	Zr(2)–B(20)	2.569(5)
Zr(1)–B(30)	2.535(5)	Zr(2)–B(40)	2.541(5)
Zr(2)–B(50)	2.442(5)	Zr(1)–B(60)	2.401(5)
Zr(1)···Zr(2)	3.1025(5)	Zr(1)–H(13)	1.91(3)
Zr(1)–H(14)	2.06(4)	Zr(1)–H(15)	1.96(4)
Zr(2)–H(13)	2.03(3)	Zr(2)–H(14)	1.94(4)
Zr(2)–H(15)	1.95(4)	Zr(1)–H(1)	2.04(4)
Zr(1)–H(2)	2.02(4)	Zr(1)–H(5)	2.05(3)
Zr(1)–H(6)	2.05(4)	Zr(1)–H(11)	1.96(4)
Zr(1)–H(12)	2.03(4)	Zr···H(65A)	2.579(4)
Zr···H(55A)	2.743(4)	Zr···H$_{α(average)}$	3.742
B(10)–H(1)	1.24(4)	B(10)–H(2)	1.26(4)
B(20)–H(3)	1.20(4)	B(20)–H(4)	1.17(4)
B(30)–H(5)	1.22(4)	B(30)–H(6)	1.19(4)
K–O(1)	2.707(4)	K–O(2)	2.710(4)
K–O(3)	2.702(4)	K–O(4)	2.672(5)
B(60)–Zr(1)–B(30)	102.07(16)	B(60)–Zr(1)–B(10)	114.71(16)
B(30)–Zr(1)–B(10)	105.15(16)	B(60)–Zr(1)–Zr(2)	113.48(12)
B(30)–Zr(1)–Zr(2)	115.73(11)	B(10)–Zr(1)–Zr(2)	105.70(11)
H(1)–Zr(1)–H(2)	56.7(17)	H(1)–B(10)–H(2)	100(3)
H(5)–Zr(1)–H(6)	55.2(15)	H(5)–B(30)–H(6)	104(3)
H(11)–Zr(1)–H(12)	55.4(16)	H(11)–B(60)–H(12)	99(3)
C(15)–B(10)–Zr(1)	131.3(3)	C(11)–B(10)–Zr(1)	120.6(3)
C(21)–B(20)–Zr(2)	129.6(3)	C(25)–B(20)–Zr(2)	122.5(3)
C(35)–B(30)–Zr(1)	113.3(3)	C(31)–B(30)–Zr(1)	138.4(3)
C(41)–B(40)–Zr(2)	132.4(3)	C(45)–B(40)–Zr(2)	119.7(3)
C(51)–B(50)–Zr(2)	154.9(3)	C(55)–B(50)–Zr(2)	95.6(3)
C(61)–B(60)–Zr(1)	159.5(3)	C(65)–B(60)–Zr(1)	91.8(3)

significantly shorter than the Zr · Zr distances in dinuclear zirconium complexes with two bridging hydrogens, {HN(SiMe$_2$C$_2$H$_4$)$_2$Zr(μ-H)H}$_2$ (3.462(1) Å) [18], {[Me$_2$Si-(C$_5$Me$_4$)$_2$]Zr(H)(μ-H)}$_2$ (3.5503(4) Å) [19], [Cp$_2$Zr(O-SO$_2$CF$_3$)(μ-H)]$_2$ · 0.5THF (3.4865(1) Å) [20], [(C$_5$H$_4$CH$_3$)$_2$-Zr(μ-H)H]$_2$ (3.4599(2) Å) [21]. The Zr–H$_b$ distances in the bridging hydrides range from 1.91(3) Å to 2.06(4) Å, the average of Zr–H$_b$ distance (1.98(4) Å) is similar to those in Zr$_2$H(μ-H)$_3$(BH$_4$)$_4$(dmpe)$_2$ (1.95(3) Å) [7f], Zr$_2$(μ-H)$_3$-(BH$_4$)$_5$(PMe$_3$)$_2$ (1.92(4) Å) [7g]. The average angle of Zr–H$_b$–Zr (103°) is smaller than those in Zr$_2$H(μ-H)$_3$-(BH$_4$)$_4$(dmpe)$_2$ (107°) [7f], Zr$_2$(μ-H)$_3$(BH$_4$)$_5$(PMe$_3$)$_2$ (110°) [7g], but significantly larger than an acute Zr–H–Zr angle of 85.9° in another triple-hydride-bridged zirconium complex, (C$_5$Me$_5$)$_2$Zr$_2$(μ-H)$_3$Cl$_3$(PMe$_3$) [17].

There are two *agostic* interactions between the α-C–H hydrogens (H(65A) and H(55A)) on two of the 9-BBN hydroborate ligands and each of the zirconium metal centers. Distances are 2.579(4) Å (Zr···H(65A)) and 2.743(4) Å (Zr···H(55A)), longer than those in some complexes we reported earlier, Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_4$ [9] (2.436(9) Å, 2.551(9) Å, and 2.656(11) Å), and CpZr(Cl){(μ-H)$_2$-BC$_8$H$_{14}$}$_2$ (2.31(3) Å) [15]. But they are significantly shorter than the average distances (3.742 Å) between zirconium and the other α-C–H hydrogens ligands in this complex. Because of the limitation of the X-ray diffraction method for the determination of the hydride atom position, to obtain additional evidence for agostic interactions between the α-C–H hydrogens on the 9-BBN hydroborate ligands

and zirconium metal center, we also considered distances between Zr and C$_α$ on the 9-BBN hydroborane ligands, Zr and B, and more importantly, we also considered Zr–B–C$_α$ angles and ZrH$_2$ and H$_2$B dihedral angles in this complex. The distances of Zr(1)–C(65) (3.056 Å) and Zr(2)–C(55) (2.935 Å) on the 9-BBN hydroborate ligands with α-*agostic* hydrogen are significantly shorter than other Zr–C$_α$ distances (3.759 Å, average) where there is no apparent α-agostic hydrogen. And the distances of Zr(1)–B(60) (2.401(5) Å) and Zr(2)–B(50) (2.442(5) Å) on the 9-BBN hydroborate ligands with α-*agostic* hydrogen are shorter than other Zr–B distances (2.558(5) Å, average) with no α-*agostic* hydrogen. Furthermore, the angles of Zr(1)–B(60)–C(65) (91.80°) and Zr(2)–B(50)–C(55) (95.01°) are much smaller than those angles (132.23°) where no apparent agostic hydrogen is involved. Finally, the dihedral angles of Zr(1)–H(11)H(12)–B(60) (136.75°) and Zr(2)–H(9)H(10)–B(50) (137.65°) are much smaller than the corresponding ZrH$_2$ and H$_2$B dihedral angles with no α-C–H hydrogen on BBN ligands, Zr(1)–H(1)H(2)–B(10) (176.14°), Zr(1)–H(5)H(6)–B(30) (163.12°), Zr(2)–H$_3$H$_4$–B(20) (172.17°) and Zr(2)–H(7)H(8)–B(40) (167.45°).

4. Concluding remarks

The anionic dinuclear triple-hydrogen-bridged 9-BBN hydroborate zirconium(IV) complex [K(Et$_2$O)$_4$]-[{(μ-H)$_2$BC$_8$H$_{14}$}$_3$Zr(μ-H)$_3$Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_3$] with two α-C–H···Zr *agostic* interactions has been prepared. Based on a single-crystal X-ray structure analysis, α-C–H hydrogens on the BC$_8$H$_{14}$ unit of the 9-BBN hydroborate ligand form *agostic* interactions with the zirconium atoms in this complex. As previously discussed in the agostic interactions in the complexes Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(OEt$_2$) and Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(PhNH$_2$) [22], several criteria must be considered for the existence of an *agostic* interaction. Such as a "short" metal–hydrogen distance; a "short" metal–carbon or boron distance; a reduced bond angle M–C–C or M–B–C and a reduced dihedral angle between the M$_2$H$_2$ and H$_2$B planes. The anionic triple-hydrogen-bridged 9-BBN hydroborate zirconium(IV) complex, [K(Et$_2$O)$_4$][{(μ-H)$_2$BC$_8$H$_{14}$}$_3$Zr(μ-H)$_3$Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_3$], reported here is well within the criteria for *agostic* interactions.

Appendix A. Supplementary material

CCDC 281796 contains the supplementary crystallographic data for [K(Et$_2$O)$_4$][{(μ-H)$_2$BC$_8$H$_{14}$}$_3$Zr(μ-H)$_3$Zr{(μ-H)$_2$BC$_8$H$_{14}$}$_3$]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retriev-

ing.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.034.

References

[1] (a) Reviews of synthesis, characterization, reaction, and theoretical studies of transition metal hydrides, see: L. Andrews, Chem. Soc. Rev. 33 (2004) 123;
(b) G.S. McGrady, G. Guilera, Chem. Soc. Rev. 32 (2003) 383;
(c) A.J. Hoskin, D.W. Stephan, Coord. Chem. Rev. 233–234 (2002) 107;
(d) J.-E. Bäckvall, J. Organomet. Chem. 652 (2002) 105;
(e) M. Peruzzini, R. Poli (Eds.), Recent Advances in Hydride Chemistry, Elsevier, New York, 2001;
(f) R.B. King, Coord. Chem. Rev. 200–202 (2000) 813;
(g) F. Maseras, A. Liedós, E. Ciot, O. Eisenstein, Chem. Rev. 100 (2000) 601;
(h) V.D. Markhaev, Russ. Chem. Rev. 69 (2000) 727;
(i) R. Bau, M.H. Drabnin, Inorg. Chim. Acta 259 (1997) 27;
(j) Z. Xu, Z. Lin, Coord. Chem. Rev. 156 (1996) 139;
(k) R.H. Grubbs, G.W. Coates, Acc. Chem. Res. 29 (1996) 85;
(l) A. Dedieu (Ed.), Transition Metal Hydrides, VCH, New York, 1992;
(m) G. Ohanessian, W.A. Goddard, Acc. Chem. Res. 23 (1990) 386;
(n) M. Brookhart, M.L.H. Green, L.-L. Wong, Prog. Inorg. Chem. 36 (1988) 1;
(o) A.G. Ginzhurg, Russ. Chem. Rev. 57 (1988) 1175;
(p) R.G. Teller, R. Bau, Struct. Bond. 44 (1981) 1;
(q) P. Wolczanski, J.E. Bercaw, Acc. Chem. Res. 13 (1980) 121.
[2] P.C. Wailes, H. Weigold, J. Organomet. Chem. 24 (1970) 405.
[3] D.W. Hart, J. Schwartz, J. Am. Chem. Soc. 96 (1974) 8115.
[4] (a) Review articles for synthesis and reactions of Cp$_2$Zr(H)Cl, see: P. Wipf, H. Jahn, Tetrahedron 52 (1996) 12853;
(b) D.J. Cardin, M.F. Lappert, C.L. Raston, Chemistry of Organo-Zirconium and Hafnium Compounds, Ellis Horwood, Chichester, England, 1986 (Chapter 20);
(c) J. Schwartz, F.T. Dayrit, J.S. Temple, In: B.M. Trost, C.R. Hutchinson (Eds.), Organic Synthesis Today and Tomorrow, Pergamon Press, Oxford, 1981;
(d) J. Schwartz, J.A. LabingerNew Synthetic Methods, vol. 5, Verlag-Chemie, New York, 1979;
(e) J. Schwartz, J.A. Labinger, Angew. Chem. 88 (1976) 402.
[5] (a) Examples for organic reactions of Cp$_2$Zr(H)Cl, see: D. Strand, T. Rein, Org. Lett. 7 (2005) 199;
(b) H. Li, P.J. Walsh, J. Am. Chem. Soc. 126 (2004) 6538;
(c) X. Huang, D. Duan, W. Zheng, J. Org. Chem. 68 (2003) 1958;
(d) F. Richter, M. Bauer, C. Perez, C. Maichle-Mössmer, M.E. Maier, J. Org. Chem. 67 (2002) 2474;
(e) K. Fujita, T. Nakamura, H. Yorimitsu, O.K. shima, J. Am. Chem. Soc. 123 (2001) 3137;
(f) L.A. Watson, D.V. Yandulov, K.G. Caulton, J. Am. Chem. Soc. 123 (2001) 603;
(g) N. Dufour, J.-P. Majoral, A.-M. Caminade, R. Choukroun, Y. DromzC, Organometallics 10 (1991) 45;
(h) I. Hyla-Krystpin, R. Gleiter, C. Kruger, R. Swettler, G. Erker, Organometallics 9 (1990) 517;
(i) J.-P. Majoral, N. Dufour, F. Meyer, A.-M. Caminade, J. Chem. Soc., Chem. Commun. (1990) 507;
(j) E. Uhlig, B. BUrglen, C. Krtiger, P. Betz, J. Organomet. Chem. 382 (1990) 77;
(k) U. Annby, S. Gronowitz, A. Hallberg, J. Organomet. Chem. 368 (1989) 295;
(l) J.E. Nelson, J.E. Bercaw, J.A. Labinger, Organometallics 8 (1989) 2483;
(m) T. Gibson, Organometallics 6 (1987) 918;
(n) T. Kunieda, T. Mori, T. Higuchi, M. Hirobe, Tetrahedron Lett. 26 (1985) 1977;
(o) A. Chiesi-Villa, C. Guastini, J. Am. Chem. Soc. 107 (1985) 6278;
(p) G. Erker, W. Fromberg, J.L. Atwood, W.E. Hunter, Angew. Chem., Int. Ed. Engl. 23 (1984) 68.
[6] G. Erker, R. Schlund, C. Krüger, Organometallics 8 (1989) 2346.
[7] (a) T. Matsuo, H. Kawaguchi, Organometallics 22 (2003) 5379;
(b) L. Jia, E. Ding, A.L. Rheingold, B. Rhatigan, Organometallics 19 (2000) 963;
(c) H. Basch, D.G. Musaev, K. Morokuma, M.D. Fryzuk, W.W. Love, A. Albinati, T.F. Koetzle, W.T. Klooster, S.A. Mason, J. Eckert, J. Am. Chem. Soc. 121 (1999) 523;
(d) M.D. Fryzuk, J.B. Love, S.J. Rettig, V.G. Young, Science 275 (1997) 1445;
(e) L. Chen, F.A. Cotton, Inorg. Chim. Acta 257 (1997) 105;
(f) J. Gozum, S.R. Wilson, G.S. Girolami, J. Am. Chem. Soc. 114 (1992) 9483;
(g) J. Gozum, G.S. Girolami, J. Am. Chem. Soc. 113 (1991) 3829.
[8] F.-C. Liu, J. Liu, E.A. Meyers, S.G. Shore, J. Am. Chem. Soc. 122 (2000) 6106.
[9] E. Ding, B. Du, E.A. Meyers, S.G. Shore, M. Yousufuddin, R. Bau, Inorg. Chem. 44 (2005) 2459.
[10] R. Köster, G. Seidel, Inorg. Synth. 22 (1983) 198.
[11] Z. Otwinowski, W. Minor, in: C.W. CarterJr., R.M. Sweet (Eds.), Methods in Enzymology, vol. 276A, Academic Press, New York, 1997, p. 307.
[12] (a) R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33;
(b) R.H. Blessing, J. Appl. Crystallogr. 30 (1997) 421.
[13] S. Mackay, C.J. Gilmore, C. Edwards, M. Tremayne, N. Stuart, K. Shankland, A Computer Program for the Solution and Refinement of Crystal Structures from Diffraction Data, University of Glasgow, Scotland, Nonius BV, Delft, The Netherlands, and Mac-Science Co. Ltd., Yokohama, Japan, 1998.
[14] SHELXTL (version 5.10), Bruker Analytical X-ray systems, 1997.
[15] E. Ding, F.-C. Liu, E.A. Meyers, S.G. Shore, Inorg. Chem. 41 (2002) 5335.
[16] W.A. Howard, M.T. Tina, G. Parkin, Inorg. Chem. 34 (1995) 5900.
[17] J.R. van den Henda, B. Hessen, A. Meetsma, J.H. Teuben, Organometallics 9 (1990) 537.
[18] G. Bai, P. Müller, H.W. Roesky, I. Usón, Organometallics 19 (2000) 4677.
[19] H. Lee, P.J. Desrosiers, I. Guzei, A.L. Rheingold, G. Parkin, J. Am. Chem. Soc. 120 (1998) 3255.
[20] G.A. Luinstra, U. Rief, M.H. Prosenc, Organometallics 14 (1995) 1551.
[21] S.B. Jones, J.L. Petersen, Inorg. Chem. 20 (1981) 2889.
[22] E. Ding, B. Du, F. Liu, E.A. Meyers, S.G. Shore, Inorg. Chem. 44 (2005) 4871.