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A neutron diffraction study of $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$ Nam Nhat Ho^a, Robert Bau^{a,*}, Christine Plecnik^b, Sheldon G. Shore^{b,*},
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Abstract

The structure of $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$ has been determined by single-crystal neutron diffraction methods. The geometrical parameters of the central four-atom core, $\text{Ti}(\mu\text{-H})_2\text{B}$, are: $\text{Ti-H} = 1.904(15), 1.933(17)$ Å; $\text{B-H} = 1.298(15), 1.333(13)$ Å; $\text{Ti-H-B} = 94.1(8)^\circ, 96.7(9)^\circ$; $\text{H-Ti-H} = 65.3(6)^\circ, \text{H-B-H} = 103.8(9)^\circ$; $\text{Ti}\cdots\text{B} = 2.426(12)$ Å; $\text{H}\cdots\text{H} = 2.071(19)$ Å. The final weighted agreement factor is $R_w = 8.7\%$ for 2635 unique reflections collected at 20 K from a crystal of volume 0.8 mm^3 at the Argonne Intense Pulsed Neutron Source (IPNS). This structure determination represents the first neutron diffraction analysis of a Ti–H bonding distance in a molecule, as well as the first neutron analysis of a Ti–H–B bridge bond. © 2002 Published by Elsevier Science B.V.

Keywords: Neutron diffraction; Titanium; Borohydride; Metal hydride; M–H–B bridge bond

1. Introduction

There has been a growing interest in the interaction of boranes with organotransition metal compounds, especially in regard to their role in transition metal catalyzed hydroboration and various B–C bond formation reactions [1,2]. Although organotitanium compounds [3] have received particular attention in this regard, their molecular structures have not been studied by the neutron diffraction technique to date. Several recent X-ray studies have succeeded in locating, and in a few cases refining, hydrogen atom positions, but it is clear that such studies are on the whole unable to generate hydrogen positions with the sufficiently high precision necessary to reveal the detailed geometry of M–H–B bonds. Recently, we have prepared several complexes of cyclic organohydroborate ligands to titanocene [4], and in this paper the first neutron diffraction study of a Ti–H–B bridge bond, in the complex $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$, is reported. This organotitaniumhydroborate compound is an example of a compound having a four-membered $\text{M}(\mu\text{-H})_2\text{B}$ ring, in which each Ti–H–B

bridge is an electron-deficient three-center two-electron bond.

2. Experimental

The title compound, $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$, was prepared through the reaction of a 1:2 molar ratio of Cp_2TiCl_2 with the potassium salt of the corresponding cyclic organohydroborate anion, $[\text{H}_2\text{BC}_8\text{H}_{14}]^-$ [4]. Crystals were obtained by dissolving the solid in toluene and slowly evaporating the solvent at room temperature (r.t.). In an inert atmosphere chamber, a dark purple (almost black) crystal with dimensions of $0.6 \times 1.1 \times 1.2\text{ mm}^3$ was covered with fluorinated grease, wrapped in aluminum foil and glued to an aluminum pin. This sample, which was very small by neutron diffraction standards (0.8 mm^3), was mounted on the single-crystal diffractometer (SCD) at the IPNS, Argonne National Laboratory and cooled to 20 K with a Displex closed-cycle helium refrigerator (Air Products and Chemicals, Inc., Model CS-202) which operated at $20(\pm 1)$ K during data collection [5]. Time-of-flight neutron diffraction data were obtained using a SCD equipped with a position-sensitive ⁶Li-glass scintillation area detector

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(30 × 30 cm²) [6]. At the IPNS, pulses of protons are accelerated into a depleted uranium target 30 times a second to produce pulses of neutrons by the spallation process. Due to the pulsed nature of the source, neutron wavelengths are determined by time-of-flight based on the de Broglie equation $\lambda = (h/m) \cdot (t/l)$, where h is Planck's constant, m is the neutron mass, and t is the time-of-flight for a flight path l , so that the entire thermal spectrum of neutrons can be used. With a position-sensitive area detector and a range of neutron wavelengths, a solid volume of reciprocal space is sampled with each stationary orientation of the sample and the detector. One histogram of data was collected to check for crystal quality and to determine the initial orientation matrix using an auto-indexing routine. Twenty-nine histograms were collected with different χ and ϕ settings and covered ca. two octants of data ($\pm h$, $+k$, $+l$). For each setting of the diffractometer angles, data were stored in three-dimensional histogram form with coordinates (x , y , t) corresponding to horizontal and vertical detector positions, and the time-of-flight, respectively. The 120 time-of-flight histogram channels were constructed with constant $\Delta t/t = 0.015$ and corresponded to wavelengths of 0.7–4.2 Å. Bragg reflections were integrated about their predicted locations and were corrected for the Lorentz factor, the incident spectrum and the detector efficiency. A wavelength-dependent spherical absorption correction was applied using cross-sections from Sears [7a] for the nonhydrogen atoms and from Howard et al. [7b] for the hydrogen atoms [7]. Symmetry-related reflections were not averaged, because different extinction factors are applicable to reflections measured at different wavelengths. Final refinement with the GSAS program [8] was performed with anisotropic atomic displacement parameters for the hydrogen atoms and isotropic parameters for non-hydrogen atoms. Data collection and refinement parameters are summarized in Table 1, selected distances and angles are given in Table 2, and a molecular plot is shown in Fig. 1.

3. Discussion

Boron compounds are usually considered to be poorly suited for neutron diffraction analysis due to the high thermal neutron absorption coefficient of the ¹⁰B isotope, a property that makes this nuclide useful as the key component of control rods in many nuclear reactors [9], but that introduces undesirably high absorption factors in crystallographic analysis. Consequently, accurate measurements of the dimensions of B–H, B–H–B and B–H–M bonds are often difficult to obtain using this technique [10]. Indeed, the only example of a binary boron hydride studied with the neutron diffraction method is a sample of B₁₀H₁₄

Table 1
Crystal data and parameters for data collection for Cp₂Ti{(μ-H)₂BC₈H₁₄}^a

Empirical formula	C ₁₈ H ₂₆ BTi
Formula Weight (amu)	301.10
Temperature (K)	20 K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	10.9050(10)
<i>b</i> (Å)	7.9126(7)
<i>c</i> (Å)	18.1110(20)
α (°)	90.0
β (°)	91.770(10)
γ (°)	90.0
<i>V</i> (Å ³)	1562.00(26)
<i>Z</i>	4
Crystal size (mm)	1.1 × 1.2 × 0.6
Transmission factors (max/min)	0.752/0.413
Unique reflections (all data/3 σ data)	2635/1925
Final <i>R</i> indices [<i>I</i> > 3 σ (<i>I</i>)]	<i>R</i> = 0.101, <i>R</i> _w = 0.084
<i>R</i> indices (all data)	<i>R</i> = 0.114, <i>R</i> _w = 0.087
Goodness-of-fit	1.76

^a Estimated S.D. for the unit cell parameters were calculated using the GSAS program (reference [8]).

Table 2
Some selected bond lengths and angles in Cp₂Ti{(μ-H)₂BC₈H₁₄}

Bond lengths (Å)			
Ti–H _a	1.933(17)	B–H _a	1.333(13)
Ti–H _b	1.904(15)	B–H _b	1.298(15)
Ti···B	2.426(12)	Ti···X _a	2.050(9) ^a
H _a ···H _b	2.071(19)	Ti···X _b	2.028(10) ^a
Bond angles (°)			
Ti–H _a –B	94.1(8)	H _a –B–H _b	103.8(9)
B–H _b –Ti	96.7(9)	H _a –Ti–H _b	65.3(6)
C–B–H _a	113.1(7)	C–B–C	106.9(5)
C–B–H _b	109.5(7)	X _a –Ti–X _b	138.3(5) ^a

^a X_a and X_b are the centroids of the two Cp rings.

isotopically enriched with ¹¹B [11], which unlike ¹⁰B does not have a high neutron absorption cross-section. On the other hand, if the boron content of a compound is sufficiently low (e.g. with a mole fraction of 5–10% or lower), absorption problems will not be too severe, and a neutron diffraction analysis should be possible [12]. Despite this, only about a half dozen compounds have been analyzed to date by this method (vide infra). In this paper, we report the first neutron diffraction analysis of a titanium borohydride complex, the 17-electron paramagnetic molecule Cp₂Ti{(μ-H)₂BC₈H₁₄} [4], which also happens to be the first neutron diffraction structure determination of a titanium–hydrogen bond.

Many compounds with Ti–H–B bonds have been analyzed by X-ray diffraction techniques (Table 3). Note that there is a wide scatter of values in the reported titanium hydride bonding distances, ranging from

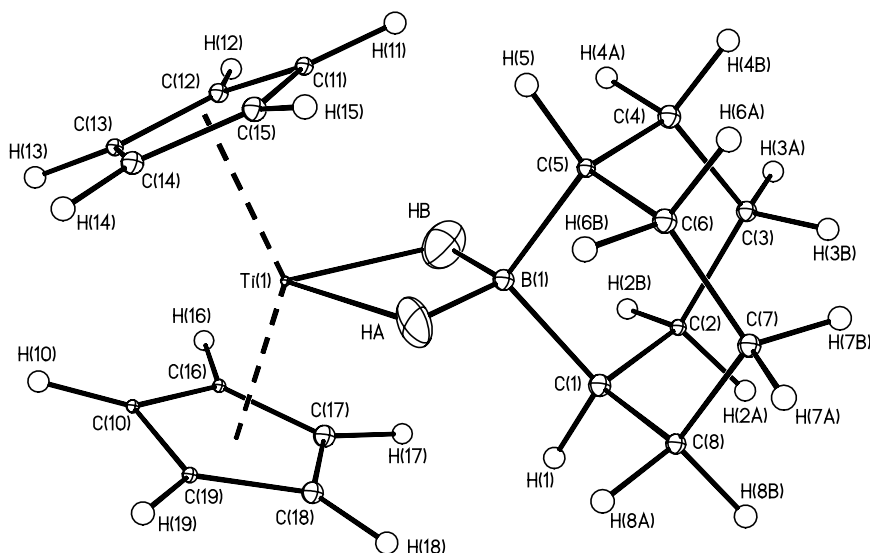


Fig. 1. Molecular plot of $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$ as obtained from the neutron diffraction analysis (ellipsoids are plotted at 70% probability, and spheres of arbitrary radius are used to represent the C–H hydrogen atoms).

1.61(5) [13] to 2.04(2) Å [14]. In our case, we have obtained the molecular structure of $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$ with Ti–H bonding distances of 1.933(17) and 1.904(15) Å, respectively, which turn out to be very close to the values determined earlier in the X-ray analysis [1.89(2) and 1.90(1) Å] [4]. In Table 3, a comparative chart is shown in which several Ti–H–B bridging compounds are listed along with the title compound.

In Table 4, we summarize the results of neutron diffraction analyses reported thus far on metal–borohydride complexes. They can be characterized as belonging to either one of three types: unidentate $[\text{M}(\mu\text{-H})\text{BH}_3]$, bidentate $[\text{M}(\mu\text{-H})_2\text{BH}_2]$, and tridentate $[\text{M}(\mu\text{-H})_3\text{BH}]$, which appear in the table as bond types 1, 2 and 3, respectively. It is difficult to make generalizations based on such a small number of samples, but one trend that

can be readily discerned is the M–H–B angle as a function of number of bridging hydrogens. As we go along the series $[\text{M}(\mu\text{-H})\text{BH}_3]$, $[\text{M}(\mu\text{-H})_2\text{BH}_2]$ and $[\text{M}(\mu\text{-H})_3\text{BH}]$, one sees a distinct decrease in the M–H–B angle (from 100–122 to 89–98 to 80–83°). In addition, the compounds $\text{Cu}(\text{PPh}_2\text{Me})_3(\text{BH}_4)$ (unidentate) [18] and $\text{Cu}(\text{PPh}_3)(\text{phen})(\text{BD}_4)$ (pseudo-unidentate) [19] are especially intriguing. $\text{Cu}(\text{PPh}_3)(\text{phen})(\text{BD}_4)$ has a highly unsymmetrical bidentate bridge [$\text{Cu}\text{-D} = 1.63(7)$ and $2.03(9)$ Å], and represents an intermediate situation (*Ia*) between a truly unidentate borohydride ligand such as the one found in $\text{Cu}(\text{PPh}_2\text{Me})_3(\text{BH}_4)$ [$\text{Cu}\text{-H} = 1.697(5)$ and $\text{Cu}\cdots\text{H} = 2.722(7)$ Å] (*I*) and a symmetrical $\text{M}(\mu\text{-H})_2\text{B}$ bridge (*II*) as found in the title compound of this paper. In fact, the pattern of M–H–B bonds in Table 4 is suggestive of a sequence of ‘stopped action’ photographs [24] as the $[\text{BH}_4]^-$ unit approaches the metal

Table 3
Comparison of distances in Ti–H–B bridged complexes

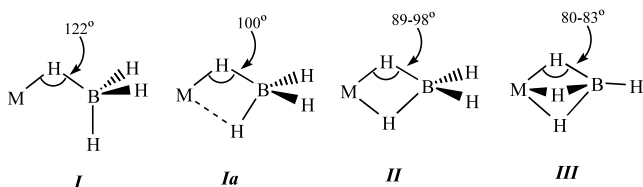
Complex	Ti–H (Å)	B–H (Å)	Ti \cdots B (Å)	Method	References
$\text{Cp}_2\text{Ti}(\text{HBO}_2\text{C}_6\text{H}_3\text{F})(\text{Pme}_3)$	1.61(5)	1.35(5)	2.267(6)	X	[13]
$\text{Cp}_2\text{Ti}(\text{BH}_4)$	1.75(8)	1.23(8)	2.37(1)	X	[16]
$\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$	1.83(3) 1.84(4)	1.23(3) 1.27(3)	2.409(4)	X	[4]
$\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$	1.88(3) 1.88(4)	1.18(3) 1.35(3)	2.446(3)	X	[4]
$\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$	1.89(2) 1.90(1)	1.23(1) 1.29(2)	2.428(2)	X	[4]
$\text{Ti}(\text{BH}_4)_3(\text{Pme}_3)_2$	1.90(6)	1.03(7)	2.40(1)	X	[17]
$\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$	1.904(15) 1.933(17)	1.333(13) 1.298(15)	2.426(12)	N	^a
$\text{Cp}_2\text{Ti}[\eta^2\text{-H}_2\text{B}(\text{C}_6\text{F}_5)_2]$	2.03 1.97	1.32 1.32	2.450(10)	X	[15]
$\text{Ti}(\text{BH}_4)_2(\text{dmpe})_2$	2.04(2) 2.09(2)	1.14(2), 1.16(2)	2.534(3)	X	[14]

^a This work.

Table 4

A summary of measurements of bridging hydrogen positions in various boron containing molecules, obtained from neutron diffraction analyses

Compound	Bond type ^a	M–H (Å)	M–H–B (°)	M–B (Å)	B–H(br) (Å)	H–M–H (°)	H–B–H (°)	H···H (Å)	References
Cu(PPh ₂ Me) ₃ (BH ₄)	1	1.697(5)	121.7(4)	2.518(3)	1.170(5)			2.023	[18]
Cu(PPh ₃)(phen)(BD ₄) ^b	1 ^c	1.63(7)	100(2)	2.29(2)	1.21(3)		112(2)	2.00	[19]
[U(BH ₄) ₄] _n	2	2.41(2)	98(1)	2.86(2)	1.25(4)	50.6	113.5	2.09	[20]
Hf(C ₅ H ₄ Me) ₂ (BH ₄) ₂	2	2.095(8)	96.8(5)	2.553(6)	1.232(11)	57.0(3)	108.4(6)	2.00	[21]
TiCp ₂ {(μ-H) ₂ BC ₈ H ₁₄ }	2	1.933(17)	94.1(8)	2.426(12)	1.333(13)	65.3(6)	103.8(9)	2.071(19)	^d
		1.904(15)	96.7(9)		1.298(15)				
Co(terpyridine)BH ₄	2	1.707(10)	90.8(6)	2.15(1)	1.298(15)	73.6(6)	106.5(6)	2.06	[22]
		1.740(12)	89.2(6)		1.290(9)				
[U(BH ₄) ₄] _n	3	2.34(2)	83(1)	2.52(1)	1.23(3)	49.8	105.3	1.96	[20]
Hf(BH ₄) ₄	3	2.130(9)	80.6(6)	2.281(8)	1.235(10)	55.1	105.8(6)	1.970(16)	[23]

^a Bond type: 1 = M(μ-H)BH₃, 2 = M(μ-H)₂BH₂, 3 = M(μ-H)₃BH.^b Phen = 1,10-phenanthroline.^c BD₄⁻ is bound asymmetrically, with Cu–D distances of 1.63(7) Å (above) and 2.03(9) Å.^d Present work.atom more and more closely (*I* → *Ia* → *II* → *III*):

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 184040 for compound Cp₂Ti{(μ-H)₂BC₈H₁₄}. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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