

# Synthesis and crystal structures of two (cyclopentadienyl)titanium(III) hydroborate complexes, [Cp\*TiCl(BH<sub>4</sub>)<sub>2</sub>] and Cp<sub>2</sub>Ti(B<sub>3</sub>H<sub>8</sub>)

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## Abstract

Treatment of Cp\*TiCl<sub>3</sub> and Cp<sub>2</sub>TiCl<sub>2</sub> with NaB<sub>3</sub>H<sub>8</sub> affords the titanium(III) hydroborate compounds [Cp\*TiCl(BH<sub>4</sub>)<sub>2</sub>] and Cp<sub>2</sub>Ti(B<sub>3</sub>H<sub>8</sub>), respectively. The former compound arises by means of a new reaction, the metal-induced fragmentation of the B<sub>3</sub>H<sub>8</sub> anion, and can also be made by treating Cp\*TiCl<sub>3</sub> with LiBH<sub>4</sub>. The latter compound has been previously described, but not characterized crystallographically. Both compounds have been studied by single crystal X-ray diffraction. Dimeric [Cp\*TiCl(BH<sub>4</sub>)<sub>2</sub>] has bridging chloride ligands and terminal Cp\* and BH<sub>4</sub> ligands. The Ti–Ti distance is 3.452(1) Å, which indicates that there is no metal–metal bonding interaction. The Ti–Cl distances are 2.440(2) Å and the Ti–Cl–Ti and Cl–Ti–Cl angles of 89.97(8) and 90.03(8)° so that the Ti<sub>2</sub>Cl<sub>2</sub> unit is nearly a perfect square. The BH<sub>4</sub> groups are each tridentate, with a Ti–B distance of 2.220(9) Å and an average Ti–H distance of 1.98(5) Å. In Cp<sub>2</sub>Ti(B<sub>3</sub>H<sub>8</sub>), the B<sub>3</sub>H<sub>8</sub> ligand is bidentate, as is usually seen, and the Ti–B and Ti–H distances are 2.600(3) and 1.96(2) Å. The dihedral angle between the Ti–B(1)–B(2) plane and the B(1)–B(2)–B(3) plane is 123.4°. The Ti–B distances are 0.04 Å longer than those in niobium analog, Cp<sub>2</sub>Nb(B<sub>3</sub>H<sub>8</sub>), despite the fact that the single bond metallic radius of Ti is 0.02 Å smaller than that of Nb. This lengthening of the bond is probably a consequence of the presence of one fewer skeletal bonding electron in Cp<sub>2</sub>Ti(B<sub>3</sub>H<sub>8</sub>). © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Titanium; Borohydride; Hydroborate; Cyclopentadienyl; Pentamethylcyclopentadienyl; Crystal structure

## 1. Introduction

Volatile transition metal tetrahydroborate complexes, M(BH<sub>4</sub>)<sub>x</sub>, are attractive CVD precursors for metal boride thin films, which are attracting interest as potential replacements for metal nitrides as copper diffusion barriers in integrated circuits [1–8]. Unfortunately, relatively few binary BH<sub>4</sub> compounds are known: for the d-block transition metals, the only known examples are Ti(BH<sub>4</sub>)<sub>3</sub> [1], Zr(BH<sub>4</sub>)<sub>4</sub> [2,3], and Hf(BH<sub>4</sub>)<sub>4</sub> [4–8]. The rarity of such compounds is in part a consequence of the small size and strong reducing power of the BH<sub>4</sub> ligand. Because the formation of volatile borohydride complexes should be favored by

employing a sterically more demanding boron hydride ligand than BH<sub>4</sub>, in the last few years we have been investigating the chemistry of the largely unexplored octahydrotriborate anion, B<sub>3</sub>H<sub>8</sub><sup>−</sup>. Our initial investigations of this approach have been highly successful: we have synthesized the previously-unknown compound Cr(B<sub>3</sub>H<sub>8</sub>)<sub>2</sub> and demonstrated that it is an excellent CVD precursor to CrB<sub>2</sub> thin films [9–11]. We also prepared several examples of cyclopentadienyl complexes containing the B<sub>3</sub>H<sub>8</sub> ligand, such as Cp\*V(B<sub>3</sub>H<sub>8</sub>)<sub>2</sub>, and Cp\*Cr(B<sub>3</sub>H<sub>8</sub>)<sub>2</sub> [12].

In some cases, the reaction of the B<sub>3</sub>H<sub>8</sub> anion with transition metal salts results in the isolation of products that contain other hydroborate ligands. For example, reaction of the pentamethylcyclopentadienyl complex [Cp\*CoCl]<sub>2</sub> with NaB<sub>3</sub>H<sub>8</sub> affords the product Cp<sub>2</sub>\*Co<sub>2</sub>(B<sub>6</sub>H<sub>14</sub>) [12]. The B<sub>6</sub>H<sub>14</sub> ligand arises by the dehydrogenative coupling

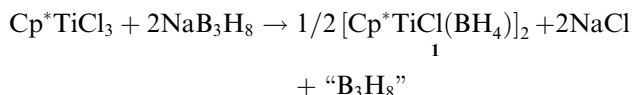
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of two  $B_3H_8$  ligands. The  $B_6H_{14}$  ligand, which adopts an S-shape, is best regarded as a dianionic bi-borallyl group  $H_3B(\mu-H)BH(\mu-H)BHBH(\mu-H)BH(\mu-H)BH_3$  in which one hydrogen at each end of the chain is involved in an agostic interaction. From a cluster point of view,  $Cp_2^*Co_2(B_6H_{14})$  is a rare example of a *hypho* cluster: it can be generated by removing three adjacent high-connectivity vertices from the 11-vertex *closo* polyhedron. Another example of the dehydrogenative coupling reaction of the  $B_3H_8$  anion is the reaction of  $[Cp^*MoCl_2]_2$  with  $NaB_3H_8$  to afford  $Cp_2^*Mo_2(B_5H_9)$  [12]. The  $B_5H_9$  ligand in this molecule adopts a planar C-shaped structure, sandwiched between the two Mo atoms.

We now describe the reactions of the cyclopentadienyl titanium compounds  $Cp^*TiCl_3$  and  $Cp_2TiCl_2$  with  $NaB_3H_8$ , which afford the products  $[Cp^*TiCl(BH_4)]_2$  and  $Cp_2Ti(B_3H_8)$ , respectively. The former compound, which arises by the metal-induced fragmentation of the  $B_3H_8$  anion, can also be made by treating  $Cp^*TiCl_3$  with  $LiBH_4$ . Both compounds have been characterized by X-ray crystallography.

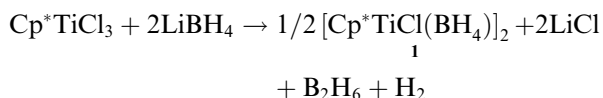
## 2. Results

We expected that treatment of the pentamethylcyclopentadienyl complex  $Cp^*TiCl_3$  with  $NaB_3H_8$  would afford a titanium  $B_3H_8$  complex, but instead yields the titanium(III) tetrahydroborate complex  $[Cp^*TiCl(BH_4)]_2$  (**1**).



This compound is the  $Cp^*$  analog of the known Cp complex  $[CpTiCl(BH_4)]_2$  [13]. Although the conversion of the  $B_3H_8$  anion to other hydroborates is known [12], the conversion to a  $BH_4$  anion is unusual. We can find only one similar reaction, in which " $B_3H_7$ " prepared in situ reacts with a transition metal complex to form a metal  $BH_4$  product [14]. A few examples of the reverse reaction have been described:  $[Mo(CO)_4(B_3H_8)]^-$  [15],  $Cp^*ReH_3(B_3H_8)$  [16], and  $WH_3(B_3H_8)(PMe_3)_3$  [17] have been prepared by treating  $[Mo_2H(CO)_{10}]^-$ ,  $Cp^*ReH_6$ , and  $WH_6(PMe_3)_3$  with  $BH_3 \cdot thf$ , respectively, and  $(C_5H_4-i-Pr)WH_3(B_3H_8)$  has been made by treating  $(C_5H_4-i-Pr)WCl_4$  with  $LiBH_4$  [18]. In addition, other  $B_3H_x$  fragments (especially those with  $x = 6$  or 7) can be made by adding  $BH_3$  to a transition metal hydride or chloride [19–28].

Compound **1** can be obtained more simply by treatment of  $Cp^*TiCl_3$  with excess  $LiBH_4$ . The product is isolated as green micro-crystals in 48% yield after crystallization from toluene.



The IR spectrum of **1** shows a strong band at  $2525\text{ cm}^{-1}$  due to a terminal B–H stretch and medium intensity bands at 2286, 2135, and  $2081\text{ cm}^{-1}$  due to metal-bridging B–H stretches; all of these bands are characteristic of tridentate  $BH_4$  ligands [29]. For comparison,  $[CpTiCl(BH_4)]_2$  shows a strong band at  $2536\text{ cm}^{-1}$  and medium intensity bands at 2276, 2233, 2136, 2127, 2068, and  $2060\text{ cm}^{-1}$  [30].

The crystal structure of  $[Cp^*TiCl(BH_4)]_2$  shows that this molecule, which resides on a site of  $2/m$  symmetry within the space group  $C2/c$ , is a dimer with bridging chloride ligands and terminal  $Cp^*$  and  $BH_4$  ligands (Fig. 1). The Ti–Ti distance is  $3.452(1)\text{ \AA}$ , which is too long for there to be significant metal–metal bonding interaction. This distance is essentially identical to that of  $3.449(1)\text{ \AA}$  in the related Cp compound  $[CpTiCl(BH_4)]_2$  [13]. The Ti–Cl distances are  $2.440(2)\text{ \AA}$  and the Ti–Cl–Ti and Cl–Ti–Cl angles of  $89.97(8)$  and  $90.03(8)^\circ$  so that the  $Ti_2Cl_2$  unit is nearly a perfect square. The  $BH_4$  groups are each tridentate, with a Ti–B distance of  $2.220(9)\text{ \AA}$  and an average Ti–H distance of  $1.98(5)\text{ \AA}$ . The terminal B–H distance of  $1.04(5)\text{ \AA}$  is shorter than the average  $1.17(5)\text{ \AA}$  B–H distance to the hydrogen atoms that bridge to the titanium center, as expected. All these distances are also very similar to those in the Cp analog.

Attempts to obtain a product from the reaction of  $CpTiCl_3$  with  $NaB_3H_8$  were unsuccessful, but treatment of the bis(cyclopentadienyl) complex  $Cp_2TiCl_2$  with  $NaB_3H_8$  in diethyl ether affords  $Cp_2Ti(B_3H_8)$  (**2**) as dark blue crystals in 65% yield. This same compound has been synthesized previously by the reaction of  $Cp_2TiCl_2$  with the cesium salt  $CsB_3H_8$  in 1,2-dimethoxyethane, followed by sublimation at  $120\text{--}150\text{ }^\circ\text{C}$  [31]. IR data for this compound have previously been reported [31].

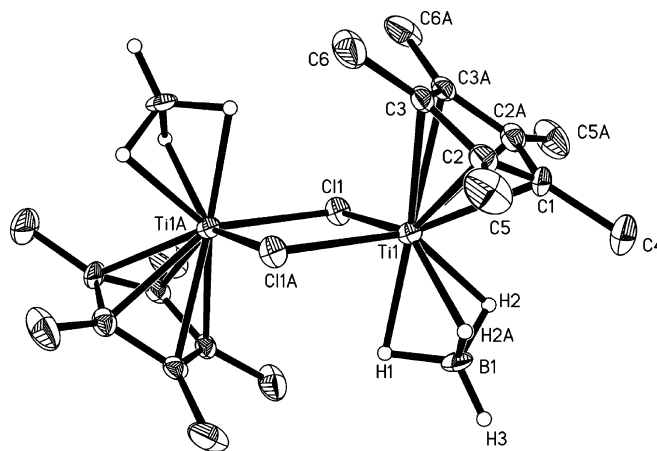
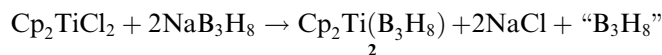


Fig. 1. ORTEP plot of  $[Cp^*TiCl(BH_4)]_2$ , (**1**). The 30% probability ellipsoids are shown, except for the hydrogen atoms which are depicted as arbitrarily-sized spheres. Hydrogen atoms on the  $Cp^*$  rings have been excluded for clarity.

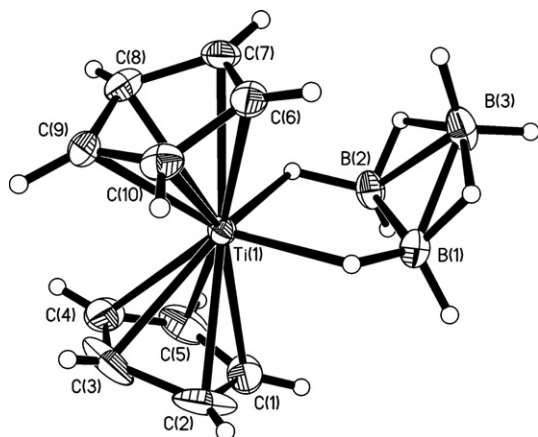


Fig. 2. ORTEP plot of  $\text{Cp}_2\text{Ti}(\text{B}_3\text{H}_8)$  (**2**). The 30% probability ellipsoids are shown, except for the hydrogen atoms which are depicted as arbitrarily-sized spheres.

Crystals of **2** conform to the space group  $P\bar{1}$  with two independent molecules in the asymmetric unit. There are no significant differences between the structures of the independent molecules, each of which adopts a bent metallocene structure. The  $\text{B}_3\text{H}_8$  ligand is bidentate (Fig. 2), and the Ti–B and Ti–H distances are 2.600(3) and 1.96(2) Å. The B–B distances within the octahydrotriborate ligand are 1.766(4), 1.811(4), and 1.817(4) Å; the first of these, which is the only B–B edge that is not bridged by a hydrogen atom, is the shortest. The dihedral angle between the Ti–B(1)–B(2) plane and the B(1)–B(2)–B(3) plane is 123.4°. The structure of **2** is very similar to that of its niobium analog,  $\text{Cp}_2\text{Nb}(\text{B}_3\text{H}_8)$  [32]. In this latter compound, the  $\text{Cp}_2\text{M}$  fragment is isolobal with the  $\text{BH}_2$  fragment, and contributes three orbitals and three electrons towards the skeletal electron count. Thus from an electron counting perspective,  $\text{Cp}_2\text{Nb}(\text{B}_3\text{H}_8)$  is the analogy of  $\text{B}_4\text{H}_{10}$ . Compound **2**, in contrast, has one fewer skeletal electron, but nevertheless adopts the same structure. The principal differences are that, in the Nb complex, the M–B distances are 0.04 Å shorter than those in **2** and the dihedral angle of 124.9° between the  $\text{MB}_2$  plane and the  $\text{B}_3$  plane is slightly larger than that in **2** (probably reflecting greater steric repulsions with the Cp ring owing to the shorter metal–ligand bond distances). The shorter M–B distances in the Nb complex are unexpected because the single bond metallic radius of Nb is actually some 0.02 Å larger than that of Ti [33]; this shortening of the bond may be a consequence of the additional skeletal bonding electron.

### 3. Experimental

All experiments were conducted under argon using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium/benzophenone immediately before use. The compounds  $\text{Cp}^*\text{TiCl}_3$  [34] and  $\text{NaB}_3\text{H}_8$  [10] were prepared according to the literature procedures. The

reagents  $\text{Cp}_2\text{TiCl}_2$  and  $\text{LiBH}_4$  were purchased from Aldrich and used as received.

Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin–Elmer 1750 infrared Fourier transform spectrometer. Melting points were measured on a Thomas Hoover capillary melting point apparatus in sealed capillaries under argon. NMR studies were carried out on General Electric QE300 and GN300NB spectrometers. Chemical shifts are reported in  $\delta$  units (positive chemical shifts to higher frequency) relative to TMS. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry at the University of Illinois.

### 3.1. Bis(pentamethylcyclopentadienyl)dichlorobis(tetrahydroborato)ditanium(III), $[\text{Cp}^*\text{TiCl}(\text{BH}_4)]_2$ (**1**)

#### 3.1.1. Procedure A

To a solution of  $\text{Cp}^*\text{TiCl}_3$  (0.39 g, 1.3 mmol) in diethyl ether (30 mL) at  $-78^\circ\text{C}$  was added a suspension of  $\text{NaB}_3\text{H}_8$  (0.26 g, 4.1 mmol) in diethyl ether (25 mL). As the mixture was warmed to room temperature, gas evolved, a white precipitate formed, and the solution color changed through bright yellow to green. The solution was stirred for 2 h at room temperature; if the solution turns brown, the reaction should be repeated and the mixture filtered while the solution is still green. The green solution was filtered and the filtrate concentrated to ca. 20 mL and cooled to  $-20^\circ\text{C}$ . After 12 h, the green microcrystals were collected by filtration and dried in vacuum. Yield: 0.1 g (33%).

#### 3.1.2. Procedure B

To a suspension of  $\text{Cp}^*\text{TiCl}_3$  (1.75 g, 6.0 mmol) in diethyl ether (50 mL) at  $-78^\circ\text{C}$  was added a solution of  $\text{LiBH}_4$  (0.40 g, 18.4 mmol) in diethyl ether (50 mL). As the mixture warmed to  $-15^\circ\text{C}$  over 40 min, the solution color changed from red to green. The mixture was kept at  $-10^\circ\text{C}$  for 2.5 h, and then the solvent was removed under vacuum. The resulting green solid was washed with pentane ( $3 \times 10$  mL) at room temperature until the washings were no longer brown. The green residue was extracted with toluene (160 mL). The extract was filtered, and the filtrate was concentrated to 100 mL and cooled to  $-20^\circ\text{C}$  to afford green microcrystals. Several additional crops of crystals could be obtained by concentration and cooling of the mother liquors, although the last crops should be examined for impurities which are indicated by the presence of extra IR bands at 2288(vs), 2222(s), and 1124(s)  $\text{cm}^{-1}$ . Yield: 0.68 g (48%). M.p.:  $>240^\circ\text{C}$ . Anal. Calc. C, 51.5; H, 8.20; Cl, 15.2; B, 4.63; Ti, 20.5. Found: C, 52.1; H, 8.29; Cl, 14.9; B, 4.69; Ti, 21.0%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta$  2.58 (s, fwhm = 35 Hz, Ti–Cp\*). IR ( $\text{cm}^{-1}$ ): 2525 s, 2286 m, 2135 m, 2081 sh, 1487 m, 1298 s, 1203 s, 1118 w, 1024 m, 723 w, 536 m.

### 3.2. Bis(cyclopentadienyl)(octahydrotriborato)-titanium(III) (2)

To a suspension of  $\text{Cp}_2\text{TiCl}_2$  (0.90 g, 3.6 mmol) in diethyl ether (40 mL) at  $-78^\circ\text{C}$  was added a solution of  $\text{NaB}_3\text{H}_8$  (0.46 g, 7.3 mmol) in diethyl ether (30 mL). As the mixture was warmed to room temperature, gas evolved, a white precipitate began to form, and the solution color changed to blue. After the solution had been stirred for 6 h at room temperature, it was filtered, and the filtrate was concentrated to saturation and cooled to  $-20^\circ\text{C}$ . After 12 h, the blue crystals were collected and dried in vacuum. Yield: 0.51 g (65 %).

### 3.3. Crystallographic studies [35]

Single crystals of  $\text{Cp}_2\text{Ti}(\text{B}_3\text{H}_8)$  (**2**) grown from diethyl ether, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to  $-75^\circ\text{C}$  in a cold nitrogen gas stream on the diffractometer. [Single crystals of  $[\text{Cp}^*\text{TiCl}(\text{BH}_4)]_2$  (**1**) grown from diethyl ether, were treated similarly. The crystal chosen was a non-merohedral twin; the diffraction patterns from the two components were easily separable and only the data from the major individual were used. Subsequent comments in brackets will refer to this compound.] Standard peak search and indexing procedures gave rough cell dimensions, and least squares refinement using 859 [461] reflections yielded the cell dimensions given in Table 1.

Table 1  
Crystal data for  $[\text{Cp}^*\text{TiCl}(\text{BH}_4)]_2$  (**1**) and  $\text{Cp}_2\text{Ti}(\text{B}_3\text{H}_8)$  (**2**)

Empirical formula	$\text{C}_{20}\text{H}_{38}\text{B}_2\text{Cl}_2\text{Ti}_2$	$\text{C}_{10}\text{H}_{18}\text{B}_3\text{Ti}$
Formula weight	466.82	218.57
$T$ (K)	193(2)	193(2)
$\lambda$ (Å)	0.71073	0.71073
Space group	$C2/m$	$P\bar{1}$
$a$ (Å)	9.167(4)	8.288(7)
$b$ (Å)	12.652(5)	11.896(10)
$c$ (Å)	11.411(5)	12.946(11)
$\alpha$ (°)	90	94.646(15)
$\beta$ (°)	112.43(7)	107.845(14)
$\gamma$ (°)	90	100.156(14)
$V$ (Å <sup>3</sup> )	1223.3(9)	1183.4(17)
$Z$	2	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.267	1.227
$\mu$ (mm <sup>-1</sup> )	0.874	0.678
Crystal size (mm)	$0.05 \times 0.10 \times 0.14$	$0.10 \times 0.28 \times 0.42$
$\theta_{\text{collection}}$ (°)	2.89–25.36	1.67–25.41
Reflections collected, unique	11438, 1177	9395, 4280
Absorption method	Face-indexed	Face-indexed
Maximum, minimum transmission factors	0.962, 0.887	0.936, 0.777
Data, restraints, parameters	1177, 0, 77	4280, 0, 397
$R_1$ [ $F_o^2 > 2\sigma(F_o^2)$ ] <sup>a</sup>	0.0592	0.0333
$wR_2$ (all data) <sup>b</sup>	0.1523	0.0813
Maximum $\Delta\rho$ (e Å <sup>-3</sup> )	0.415, -0.304	0.277, -0.274

<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$  for reflections with  $F_o^2 > 2\sigma(F_o^2)$ .

<sup>b</sup>  $wR_2 = \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2$  for all reflections.

Data were collected with an area detector by using the measurement parameters listed in Table 1. The triclinic lattice and the average values of the normalized structure factors suggested the space group  $P\bar{1}$ , which was confirmed by the success of the subsequent refinement. [For **1**, the systematic absences  $hkl$  ( $h+k \neq 2n$ ) were consistent with space groups  $C2$ ,  $Cm$ , and  $C2/m$ ; the last of these was proven to be the correct choice by the success of the subsequent refinement.] The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. Although corrections for crystal decay were unnecessary, a face-indexed absorption correction was applied, the maximum and minimum transmission factors being 0.936 and 0.777 [0.961 and 0.887]. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. All 4280 unique data were used in the least squares refinement. [For **1**, six reflections (0 0 1,  $\bar{1}$  3 7, 2 0 3, 2 4 11,  $\bar{6}$  6 11, and  $\bar{6}$  10 8) were found to be statistical outliers (the first owing to interference by the beam stop, the rest probably owing to the twinning) and were deleted; all remaining 1177 unique data were used in the least squares refinement.] (see Tables 2 and 3).

The structure was solved using direct methods (SHELXTL). Correct positions for the titanium atoms and most of the carbon and boron atoms were deduced from an E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was  $\sum w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sum (F_o^2)^2] + (0.044P)^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$  [For **1**,  $w = \{[\sum (F_o^2)^2]\}^{-1}$ ]. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. Hydrogen atoms were located in the difference maps, and their positions were refined with independent isotropic displacement parameters. [For **1**,

Table 2  
Bond lengths (Å) and angles (°) for  $[\text{Cp}^*\text{TiCl}(\text{BH}_4)]_2$  (**1**)<sup>a</sup>

Distances (Å)			
Ti(1)–Cl(1)	2.4403(17)	C(1)–C(4)	1.506(9)
Ti(1)–C(1)	2.308(7)	C(2)–C(3)	1.409(6)
Ti(1)–C(2)	2.326(5)	C(2)–C(5)	1.518(7)
Ti(1)–C(3)	2.391(4)	C(3)–C(3)''	1.396(9)
Ti(1)–B(1)	2.220(9)	C(3)–C(6)	1.513(6)
Ti(1)–H(1)	2.02(6)	B(1)–H(1)	1.06(5)
Ti(1)–H(2)	1.95(3)	B(1)–H(2)	1.29(4)
C(1)–C(2)	1.420(6)	B(1)–H(3)	1.04(5)
Angles (°)			
Cl(1)–Ti(1)–Cl(1)'	89.97(8)	H(1)–B(1)–H(2)	103(3)
Ti(1)–Cl(1)–Ti(1)'	90.03(8)	H(1)–B(1)–H(3)	120(5)
B(1)–Ti(1)–Cl(1)	103.60(19)	H(2)–B(1)–H(2)''	95(2)
H(1)–Ti(1)–H(2)	55.2(16)	H(2)–B(1)–H(3)	116(2)
H(2)–Ti(1)–H(2)''	58.1(16)		

<sup>a</sup> Symmetry transformations: ' =  $-x, -y, -z + 1$ , '' =  $x, -y, z$ .

Table 3  
Bond lengths (Å) and angles (°) for Cp<sub>2</sub>Ti(B<sub>3</sub>H<sub>8</sub>) (2)

Distances (Å)			
Ti(1)–C(1)	2.330(3)	Ti(2)–C(11)	2.340(3)
Ti(1)–C(2)	2.324(3)	Ti(2)–C(12)	2.367(3)
Ti(1)–C(3)	2.326(3)	Ti(2)–C(13)	2.372(3)
Ti(1)–C(4)	2.350(3)	Ti(2)–C(14)	2.334(3)
Ti(1)–C(5)	2.362(3)	Ti(2)–C(15)	2.337(3)
Ti(1)–C(6)	2.365(3)	Ti(2)–C(16)	2.356(3)
Ti(1)–C(7)	2.377(3)	Ti(2)–C(17)	2.322(3)
Ti(1)–C(8)	2.351(3)	Ti(2)–C(18)	2.321(3)
Ti(1)–C(9)	2.340(3)	Ti(2)–C(19)	2.355(3)
Ti(1)–C(10)	2.332(3)	Ti(2)–C(20)	2.365(3)
Ti(1)–B(1)	2.608(3)	Ti(2)–B(4)	2.616(3)
Ti(1)–B(2)	2.593(3)	Ti(2)–B(5)	2.614(3)
Ti(1)–H(11)	1.95(2)	Ti(2)–H(41)	1.92(2)
Ti(1)–H(21)	1.97(2)	Ti(2)–H(51)	1.99(2)
B(1)–B(2)	1.766(4)	B(4)–B(5)	1.767(4)
B(1)–B(3)	1.811(4)	B(4)–B(6)	1.804(4)
B(2)–B(3)	1.817(4)	B(5)–B(6)	1.813(4)
B(1)–H(11)	1.20(2)	B(4)–H(41)	1.22(2)
B(1)–H(12)	1.04(2)	B(4)–H(42)	1.09(2)
B(1)–H(13)	1.17(2)	B(4)–H(46)	1.17(2)
B(2)–H(21)	1.14(2)	B(5)–H(51)	1.12(2)
B(2)–H(22)	1.10(2)	B(5)–H(52)	1.11(2)
B(2)–H(23)	1.10(2)	B(5)–H(56)	1.12(3)
B(3)–H(13)	1.34(2)	B(6)–H(46)	1.37(2)
B(3)–H(23)	1.44(2)	B(6)–H(56)	1.40(3)
B(3)–H(31)	1.06(2)	B(6)–H(61)	1.12(2)
B(3)–H(32)	1.17(2)	B(6)–H(62)	1.11(2)
Angles (°)			
B(1)–Ti(1)–B(2)	39.70(8)	B(5)–Ti(2)–B(4)	39.50(9)
H(11)–Ti(1)–H(21)	89.0(9)	H(41)–Ti(2)–H(51)	87.9(9)
B(2)–B(1)–B(3)	61.05(16)	B(5)–B(4)–B(6)	61.02(16)
B(2)–B(1)–Ti(1)	69.69(13)	B(5)–B(4)–Ti(2)	70.18(14)
B(3)–B(1)–Ti(1)	106.44(16)	B(6)–B(4)–Ti(2)	107.03(16)
B(2)–B(1)–H(11)	114.2(9)	B(5)–B(4)–H(41)	113.3(9)
B(3)–B(1)–H(11)	124.3(10)	B(6)–B(4)–H(41)	124.7(9)
B(2)–B(1)–H(12)	113.3(12)	B(5)–B(4)–H(42)	113.7(13)
B(3)–B(1)–H(12)	124.7(12)	B(6)–B(4)–H(42)	123.1(12)
H(11)–B(1)–H(12)	108.4(15)	H(41)–B(4)–H(42)	109.5(15)
B(2)–B(1)–H(13)	108.4(12)	B(5)–B(4)–H(46)	110.4(11)
B(3)–B(1)–H(13)	47.5(12)	B(6)–B(4)–H(46)	49.5(11)
H(11)–B(1)–H(13)	102.2(15)	H(41)–B(4)–H(46)	102.6(14)
H(12)–B(1)–H(13)	109.7(17)	H(42)–B(4)–H(46)	106.4(16)
B(1)–B(2)–B(3)	60.70(16)	B(4)–B(5)–B(6)	60.49(16)
B(1)–B(2)–Ti(1)	70.61(12)	B(4)–B(5)–Ti(2)	70.32(13)
B(3)–B(2)–Ti(1)	106.84(15)	B(6)–B(5)–Ti(2)	106.81(15)
B(1)–B(2)–H(21)	115.2(11)	B(4)–B(5)–H(51)	114.2(11)
B(3)–B(2)–H(21)	122.5(11)	B(6)–B(5)–H(51)	121.1(11)
B(1)–B(2)–H(22)	111.2(11)	B(4)–B(5)–H(52)	113.7(12)
B(3)–B(2)–H(22)	123.0(12)	B(6)–B(5)–H(52)	125.1(12)
H(21)–B(2)–H(22)	111.7(16)	H(51)–B(5)–H(52)	110.7(16)
B(1)–B(2)–H(23)	113.2(12)	B(4)–B(5)–H(56)	110.8(14)
B(3)–B(2)–H(23)	52.6(12)	B(6)–B(5)–H(56)	50.4(14)
H(21)–B(2)–H(23)	98.7(16)	H(51)–B(5)–H(56)	99.4(17)
H(22)–B(2)–H(23)	105.8(17)	H(52)–B(5)–H(56)	106.8(17)
B(1)–B(3)–B(2)	58.26(15)	B(4)–B(6)–B(5)	58.49(16)
B(1)–B(3)–H(13)	40.3(11)	B(4)–B(6)–H(46)	40.2(10)
B(2)–B(3)–H(13)	98.4(11)	B(5)–B(6)–H(46)	98.6(10)
B(1)–B(3)–H(23)	95.5(10)	B(4)–B(6)–H(56)	96.6(12)
B(2)–B(3)–H(23)	37.2(10)	B(5)–B(6)–H(56)	38.2(11)
H(13)–B(3)–H(23)	135.4(15)	H(46)–B(6)–H(56)	136.6(15)
B(1)–B(3)–H(31)	113.1(13)	B(4)–B(6)–H(61)	112.7(12)
B(2)–B(3)–H(31)	113.8(13)	B(5)–B(6)–H(61)	113.0(12)
H(13)–B(3)–H(31)	101.7(16)	H(46)–B(6)–H(61)	101.3(15)
H(23)–B(3)–H(31)	102.4(15)	H(56)–B(6)–H(61)	101.5(16)

Table 3 (continued)

Angles (°)			
B(1)–B(3)–H(32)	119.7(10)	B(4)–B(6)–H(62)	119.2(12)
B(2)–B(3)–H(32)	118.5(11)	B(5)–B(6)–H(62)	120.4(12)
H(13)–B(3)–H(32)	99.5(15)	H(46)–B(6)–H(62)	98.2(15)
H(23)–B(3)–H(32)	100.7(15)	H(56)–B(6)–H(62)	102.3(16)
H(31)–B(3)–H(32)	119.1(16)	H(61)–B(6)–H(62)	118.9(16)

methyl hydrogen atoms were placed in “idealized” positions with C–H = 0.98 Å, and their displacement parameters were set equal to 1.5 times  $U_{eq}$  for the attached carbon. The hydrogen atoms on boron were located in the difference maps, and their positions were refined with a common group isotropic parameter.] No correction for isotropic extinction was necessary. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map (0.28 e Å<sup>-3</sup>) was located 0.66 Å from C3. [For **1**, the largest peak in the final Fourier difference map (0.42 e Å<sup>-3</sup>) was located 0.07 Å from Ti(1).] A final analysis of variance between observed and calculated structure factors showed no apparent errors.

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### Appendix A. Supplementary material

CCDC 669656 and 669657 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.12.017](https://doi.org/10.1016/j.jorganchem.2007.12.017).

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