



# Synthesis, and structural characterization of solvent-free divalent ytterbium bis(boratabenzene) and (cyclopentadienyl)(boratabenzene) complexes

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## ABSTRACT

The preparation and characterization of the solvent-free divalent ytterbium bis(boratabenzene) complex  $[\text{C}_5\text{H}_5\text{BCH}_2(\text{CH}_3)_2\text{P} \rightarrow \text{BC}_5\text{H}_5]_2\text{Yb}$  (**2a**) and heteroleptic complexes  $[\text{C}_5\text{H}_3\text{R}^1\text{R}^2][\text{C}_5\text{H}_5\text{BCH}_2(\text{CH}_3)_2\text{P} \rightarrow \text{BC}_5\text{H}_5]\text{Yb}$  (**3**:  $\text{R}^1 = \text{SiMe}_3$ ,  $\text{R}^2 = \text{H}$ ; **4**:  $\text{R}^1 = \text{R}^2 = \text{SiMe}_3$ ) are reported. The interactions between the pendant neutral borabenzene and the ytterbium center were observed both in the solid-state and in benzene. Addition of external  $\sigma$ -donor solvent THF to the complexes caused a dissociation of the neutral borabenzene from the ytterbium center.

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## 1. Introduction

Divalent lanthanide complexes with Cp-type ligands have fantastic reductive properties. Their redox reactions with various unsaturated substrates have witnessed tremendous progresses during the last decades [1]. Much more attentions have been drawn to the solvent-free divalent lanthanide complexes because of their much higher redox reactivities than the solvated congeners [2]. However, the synthesis of solvent-free divalent lanthanide complexes is usually difficult due to the following reasons: first of all, the preexisted solvent molecules in the starting materials, such as  $\text{SmI}_2(\text{THF})_2$ ,  $\text{YbI}_2(\text{THF})_2$ , and  $\text{EuI}_2(\text{THF})_2$ ; second, the general reaction media in synthesizing divalent lanthanide complexes are THF or ethers; third, the lanthanide metal ion is highly oxo-philic and readily coordinated by THF or ethers. Therefore, harsh conditions including the high vacuum desolvation or sublimation are generally involved in the synthesis of solvent-free divalent lanthanide complexes. For example, exposure of  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$  at 70–75 °C under a vacuum of  $5 \times 10^{-6}$  torr and subsequent increase of the temperature to 85 °C give the solvent-free divalent lanthanide complex  $(\text{C}_5\text{Me}_5)_2\text{Sm}$  [3a]. The ytterbium analogous  $(\text{C}_5\text{Me}_5)_2\text{Yb}$  and  $[1,3-(\text{CMe}_3)_2\text{C}_5\text{H}_3]_2\text{Yb}$  were prepared from their

diethyl ether adduct by toluene reflux at dynamic vacuum [3b]. The solvent-free ytterbium complex  $(\text{C}_5\text{H}_5)_2\text{Yb}$  was obtained by desolvation of  $(\text{C}_5\text{H}_5)_2\text{Yb}(\text{dme})$  at 100 °C ( $10^{-3}$  to  $4 \times 10^{-5}$  torr) and subsequent sublimation at 420 °C ( $4 \times 10^{-5}$  torr) in a sealed tube, and the structural characterization revealed a polymeric,  $\text{C}_5\text{H}_5$ -bridged zigzag chain structure, which satisfied the coordination sphere of the ytterbium center [3c].

Compared to the well-known Cp-type ligands, the heterocyclic,  $6\pi$ -electron, aromatic boratabenzene anions are weaker donors [4]. In the last three decades, increasing numbers of organometallic complexes of transition metals bearing boratabenzenes have been reported [5]. On the other hand, boratabenzene derivatives of lanthanide metals are very rare and their chemistry is remain unexplored [6,7]. Recently, we prepared several THF-solvated divalent samarium and ytterbium boratabenzene complexes,  $[(\text{C}_5\text{H}_5\text{BXPh}_2)_2\text{Sm}(\text{THF})_2]$  ( $\text{X} = \text{N}, \text{P}$ ) [8a] and  $[(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{Yb}(\text{THF})_2]$  [8b], and studied their reactivities towards methyl methacrylate polymerization or redox transformation with  $\alpha$ -diimine ligands. Bearing in mind that the solvent-free divalent lanthanide complexes are usually more reactive, the reaction of the solvent-free  $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2$  with the neutral borabenzene- $\text{PMe}_3$  adduct  $[\text{C}_5\text{H}_5\text{B} \leftarrow \text{PMe}_3]$  was studied to synthesize the solvent-free divalent ytterbium bis(boratabenzene) complex. To our surprise, a solvent-free ansa-heteroborabenzene divalent lanthanide amide (**1**) (Chart 1), which was formed via a C–H bond cleavage of  $\text{PMe}_3$  moiety, was isolated [8c,9]. One of the most significant features of

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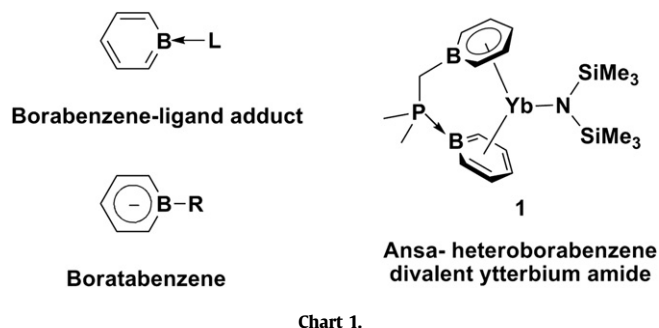


Chart 1.

the complex is the coordination of the neutral borabenzene to the ytterbium center. Preliminary reactivity studies showed that **1** reacted with N, N'-diisopropylcarbodiimide to give a divalent lanthanide guanidinate complex. In this paper, we wish to report the protonolysis reactions of **1** with cyclopentadiene and silyl-substituted cyclopentadienes, which gave the first solvent-free divalent ytterbium bis(boratabenzene) complex **2a** and heteroleptic (cyclopentadienyl)(boratabenzene) complexes **3** and **4**.

## 2. Results and discussion

### 2.1. Synthesis and characterization of divalent ytterbium bis(boratabenzene) complex

The reaction of **1** with the freshly distilled cyclopentadiene in C<sub>6</sub>D<sub>6</sub> was monitored by <sup>1</sup>H NMR spectroscopy. The reaction proceeds in a slow protonolysis of Yb-N bond to release HN(SiMe<sub>3</sub>)<sub>2</sub>, and **1** was completely consumed within 3 days. Subsequently, the reaction was scaled up in benzene, both black blocks of the divalent ytterbium bis(boratabenzene) complex (**2a**, 84% yield) and a yellow solid of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Yb (**2b**, 84% yield) were obtained after a careful workup (Scheme 1). **2a** is only sparingly soluble in benzene, the <sup>1</sup>H NMR spectrum of **2a** in C<sub>6</sub>D<sub>6</sub> revealed the presence of borabenzene ( $\delta$  = 6.73, 7.90 and 7.33 ppm for the *ortho*, *meta* and *para* protons, respectively) and boratabenzene rings ( $\delta$  = 6.57, 7.07 and 6.03 ppm for the *ortho*, *meta* and *para* protons, respectively) and a -CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub> moiety ( $\delta$  = 1.49 and 0.99 ppm).

The NMR spectroscopy data did not allow an unambiguous characterization of **2a**. Single crystals of **2a** were obtained from a benzene solution and characterized by the X-ray diffraction studies. An ORTEP diagram is shown in Fig. 1, and the selected bond lengths and angles are listed in Table 1. **2a** exhibits a bent metallocene-type structure with the central Yb ion pseudotetrahedrally coordinated by two anionic boratabenzenes and two pendant neutral borabenzenes. Inspection of the distances from the Yb ion to the boratabenzene ring (B1, C1–5) shows that the distance is longer for the Yb ion to the B1 atom (2.91 Å), but nearly identical for the Yb ion to the carbon atoms (2.79–2.83 Å), indicating an intermediate  $\eta^5$ – $\eta^6$  coordination mode between the Yb ion and the

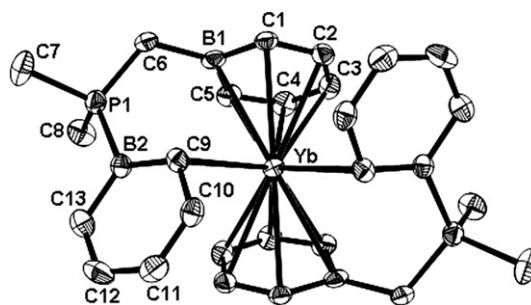
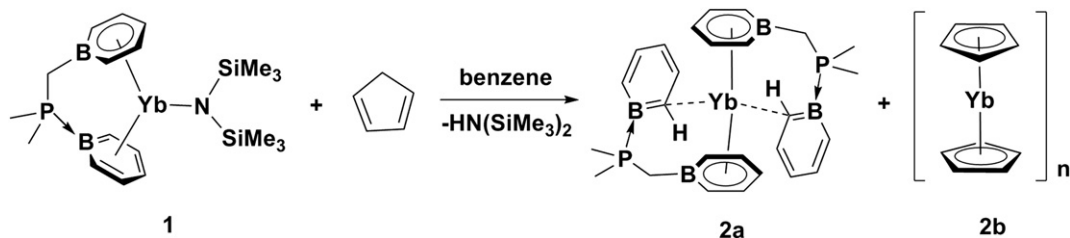


Fig. 1. Molecular structure of **2a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

boratabenzene ring. The average Yb-C (boratabenzene) distance of 2.81 Å is very close to those in **1** (2.83 Å) and [(C<sub>5</sub>H<sub>5</sub>BNPh<sub>2</sub>)<sub>2</sub>Yb(THF)<sub>2</sub>] (2.83 Å). The two pendant borabenzenes bite the Yb<sup>II</sup> ion in the front side of the metallocene wedge in a  $\eta^1$  coordination mode. The Yb-C9 bond length is 2.80 Å, which lies in the range of  $\pi$  phenyl-Yb interactions in the complex [Yb<sub>2</sub>(Odpp)<sub>4</sub>] (Odpp = 2,6-diphenylphenolate) (2.75–3.18 Å) and is close to the shortest one [10]. The short Yb-C9 bond length is also comparable to the Yb-C (olefin) separation of 2.78 Å in the Yb- $\eta^2$ -olefin complex [Yb(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -CH<sub>2</sub>CH<sub>2</sub>)PtMe<sub>2</sub>] [11]. In sharp contrast to the polymeric chain structure formed through the intermolecular Yb-Cp interactions in (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Yb, **2a** is a monomer, which can be attributed to the  $\eta^1$  interactions between the neutral borabenzene and Yb ion.

The <sup>1</sup>H NMR spectrum of **2a** in C<sub>6</sub>D<sub>6</sub> showed that such Yb–borabenzene interaction is retained in solution. The chemical shifts of the neutral borabenzene in **2a** appears at much higher field (6.73, 7.90 and 7.33 ppm for the *ortho*, *meta* and *para* protons, respectively) than those of the neutral borabenzene–ligand adduct C<sub>5</sub>H<sub>5</sub>B–PMe<sub>3</sub> (7.24, 8.04 and 7.42 ppm for the *ortho*, *meta* and *para* protons, respectively), the remarkably shift of the *ortho* protons (0.51 ppm) to the higher field implied the interaction of the *ortho* carbon of the borabenzene with the ytterbium ion. Addition of two drops of THF-*d*<sub>8</sub> to the C<sub>6</sub>D<sub>6</sub> solution of **2a** immediately changed the color of the solution from pale green to red, and caused a significant shift of the *ortho* protons of borabenzene (about 0.47 ppm) to the lower field, and slightly shifts of *meta* and *para* protons (about 0.09 and 0.13 ppm, respectively) to the higher field. The <sup>1</sup>H NMR spectrum of **2a** in neat THF-*d*<sub>8</sub> showed an even larger shift in the pendant neutral borabenzene moiety (Table 2): 7.17, 7.21 and 6.51 ppm for the *ortho*, *meta* and *para* protons of the borabenzene. These datum indicate the Yb–borabenzene interaction is retained in benzene solution, but dissociation of the borabenzene from the Yb center readily occurs when the external  $\sigma$ -donor solvent THF is added.

Multinuclear NMR spectroscopy studies of **2a** were also performed in THF-*d*<sub>8</sub>. The <sup>11</sup>B NMR spectrum showed one singlet at 34.0 ppm and one doublet at 23.9 ppm in a 1:1 ratio, while in the



Scheme 1. The protonolysis reaction of **1** with cyclopentadiene.

**Table 1**  
Selected bond lengths (Å) and angles (°) in **2a** and **4**.

	<b>2a</b>		<b>4</b>
Yb-C1	2.828(5)	Yb-B1	3.021(8)
Yb-C2	2.812(5)	Yb-C1	3.012(9)
Yb-C3	2.790(5)	Yb-C2	2.933(10)
Yb-C4	2.807(5)	Yb-C3	2.84(2)
Yb-C5	2.826(5)	Yb-C1'	2.829(11)
Yb-B1	2.908(5)	Yb-C2'	2.78(2)
Yb-C9	2.806(4)	Yb-C9	2.969(4)
C9-Yb-C9	87.2(2)	Yb-C10	2.963(4)
		Yb-C11	3.001(6)
		Yb-B2	3.039(6)
		Yb-C14	2.772(5)
		Yb-C15	2.768(3)
		Yb-C16	2.731(3)

**Table 2**  
Selected  $^1\text{H}$  NMR data (ppm) of the complexes **2a–4** at 25 °C (N: neutral borabenzene; A: anionic boratabenzene).

	Solvent	$\delta$ N <sub>ortho</sub>	$\delta$ N <sub>meta</sub>	$\delta$ N <sub>para</sub>	$\delta$ A <sub>ortho</sub>	$\delta$ A <sub>meta</sub>	$\delta$ A <sub>para</sub>	$\delta$ PCH <sub>2</sub>	$\delta$ P(CH <sub>3</sub> ) <sub>2</sub>
<b>2a</b>	C <sub>6</sub> D <sub>6</sub>	6.73	7.90	7.33	6.57	7.07	6.03	1.49	0.99
<b>2a</b>	THF- <i>d</i> <sub>8</sub>	7.17	7.21	6.51	6.50	6.81	6.31	1.83	1.36
<b>3</b>	C <sub>6</sub> D <sub>6</sub>	6.18	7.53	6.78	6.49	7.41	6.97	1.41	0.79
<b>3</b>	THF- <i>d</i> <sub>8</sub>	7.20	7.20	6.32	6.50	6.82	6.51	1.83	1.35
<b>4</b>	C <sub>6</sub> D <sub>6</sub>	6.52	7.60	6.88	6.22	7.50	7.05	1.41	0.79
<b>4</b>	THF- <i>d</i> <sub>8</sub>	7.31	7.18	6.44	6.51	6.76	6.47	1.77	1.31

$^{31}\text{P}$  NMR spectrum, only one broad doublet at  $-12.6$  ppm was observed. Although the  $^{11}\text{B}$  NMR and  $^{31}\text{P}$  NMR signals of **2a** are very close to those of **1** ( $^{11}\text{B}$  NMR:  $\delta = 33.8$  and  $25.8$  ppm;  $^{31}\text{P}$  NMR:  $\delta = -14.6$  ppm), the  $^{171}\text{Yb}$  NMR signal of **2a** ( $\delta = 142$  ppm) shifts to much higher field in comparison with that of **1** ( $\delta = 1175$  ppm).

## 2.2. Synthesis and characterization of divalent ytterbium (cyclopentadienyl)(boratabenzene) complexes

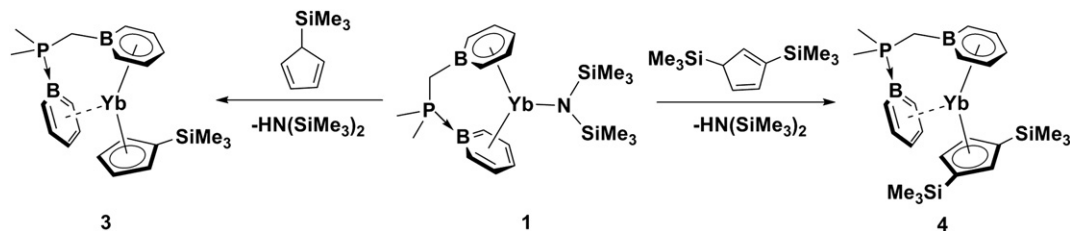
Obviously, the formation of the homoleptic complexes **2a** and **2b** is resulted from a ligand redistribution reaction of the heteroleptic (cyclopentadienyl)(boratabenzene) complex, which was generated by the protonolysis of the Yb-N bond in **1**. Considering that the sterically bulky ligands are usually effective to suppress the ligand redistribution process, the reaction of **1** with 1-trimethylsilylcyclopentadiene was subsequently studied. Reaction of **1** with 1-trimethylsilylcyclopentadiene in benzene for 2 days gave a green solution, from which the divalent ytterbium (1-trimethylsilylcyclopentadienyl)(boratabenzene) complex **3** was isolated as a green solid in 84% yield (Scheme 2). Once isolated, **3** is only sparingly soluble in benzene. The  $^1\text{H}$  NMR spectrum of **3** in C<sub>6</sub>D<sub>6</sub> exhibited broad signals for the borabenzene ( $\delta = 7.53$ ,  $6.78$  and  $6.18$  ppm) and boratabenzene ( $\delta = 7.41$ ,  $6.97$  and  $6.49$  ppm) rings, and two doublets for the  $-\text{CH}_2\text{P}(\text{CH}_3)_2$  moiety ( $\delta = 1.41$  and  $0.79$  ppm). The signals of the  $1-\text{SiMe}_3\text{C}_5\text{H}_4$  ligand appear as two triplets at  $6.36$  and  $6.20$  ppm, and one singlet at  $0.39$  ppm. The  $^1\text{H}$  NMR spectroscopy datum clearly indicated the formation of the heteroleptic

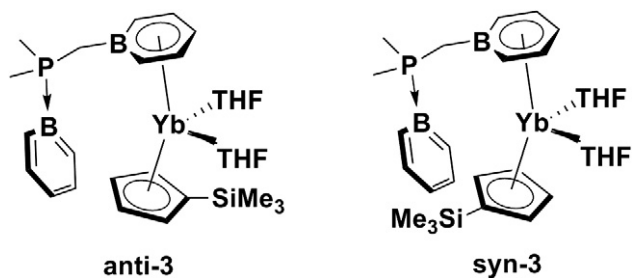
complex. The efforts to obtain the single crystals of **3** were hindered by the ligand redistribution reaction: recrystallization of pure sample of **3** in toluene or a toluene–hexane mixture at  $-35$  °C only gave the single crystals of homoleptic complex **2a**.

We are interested in the issue whether the neutral borabenzene in **3** has some interactions with the ytterbium center as that in **2a**. Although solid-state structural characterization of **3** is unavailable, studies of the solution behavior of **3** provide some convincing evidences for such interactions. Firstly, as those observed in **2a**, the  $^1\text{H}$  NMR spectrum of **3** in C<sub>6</sub>D<sub>6</sub> showed that the signals of neutral borabenzene appear at higher field ( $6.18$ ,  $7.53$  and  $6.78$  ppm for the *ortho*, *meta* and *para* protons, respectively) than those of C<sub>5</sub>H<sub>5</sub>B←PMe<sub>3</sub>. Secondly, when two drops of THF-*d*<sub>8</sub> were added to **3** in C<sub>6</sub>D<sub>6</sub>, the color of the solution changed immediately from green

to red. The signals of the anionic boratabenzene ring shift only marginally, however, those for the neutral borabenzene ring shift dramatically: the signals for the *ortho* protons of borabenzene shifts from  $6.18$  ppm to  $6.50$  ppm, the *meta* protons from  $7.53$  ppm to  $7.82$  ppm, and the *para* proton from  $6.78$  ppm to  $7.11$  ppm. The shift of signals to the lower field revealed a dissociation of the neutral borabenzene from the ytterbium center.

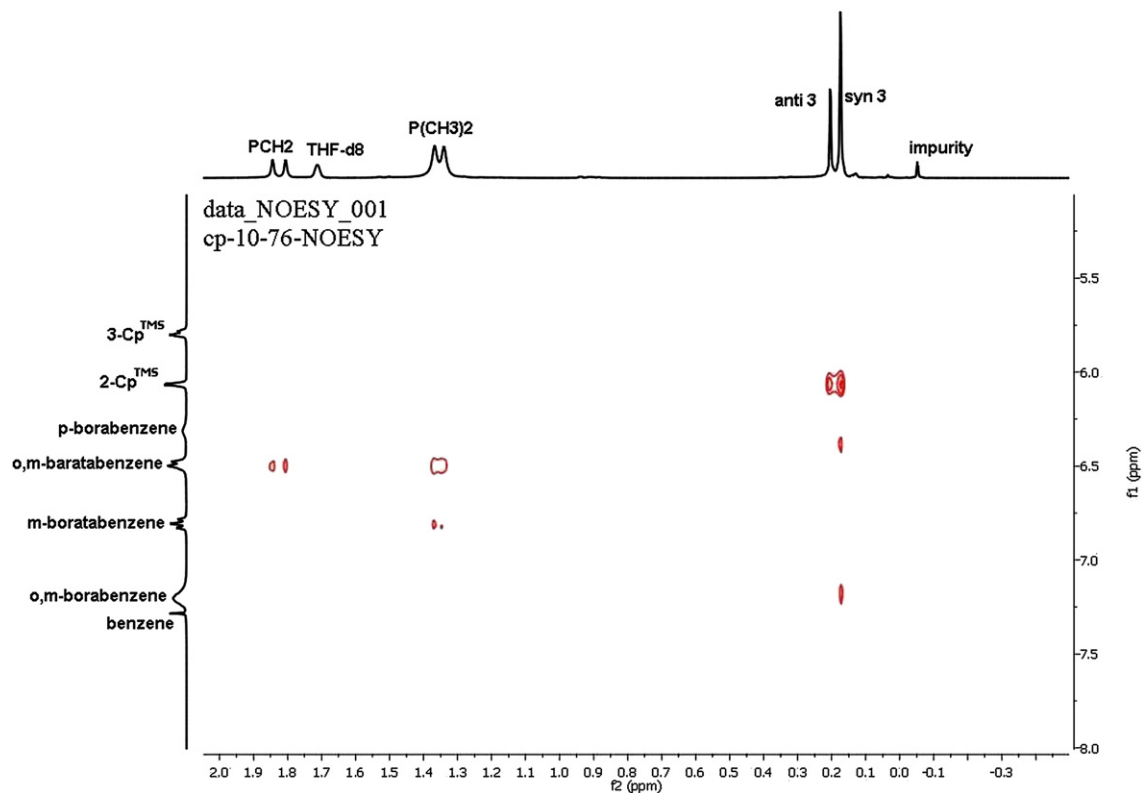
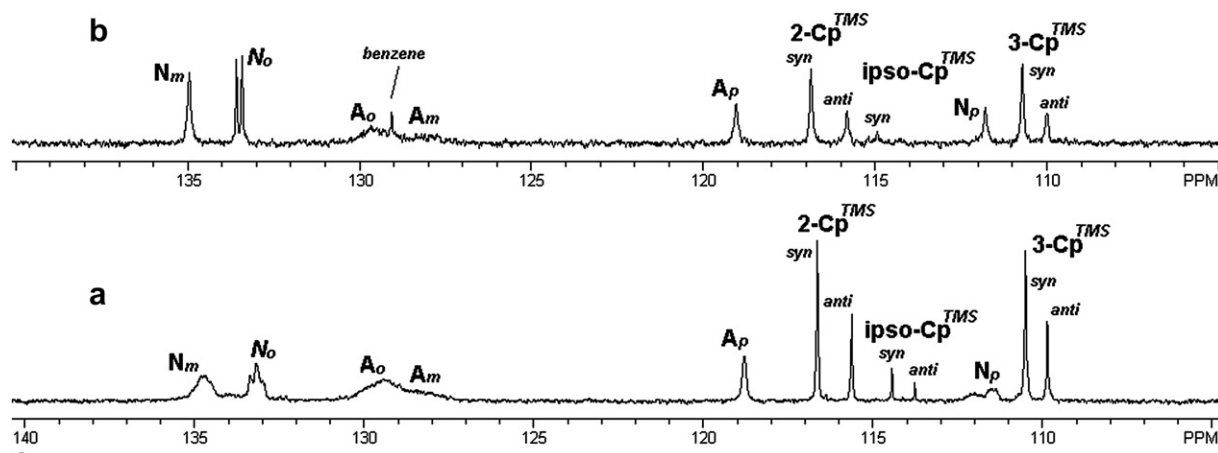
After the addition of THF-*d*<sub>8</sub> to **3** in C<sub>6</sub>D<sub>6</sub>, the 1-trimethylsilylcyclopentadienyl ligand clearly exhibited two sets of triplets ( $6.44/6.34$  and  $6.08/5.98$  ppm) and singlets ( $0.50/0.45$  ppm) in about 1:2 ratio at room temperature. Similarly, the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **3** in neat THF-*d*<sub>8</sub> showed two sets of signals for the 1-trimethylsilylcyclopentadienyl ligand ( $^1\text{H}$  NMR:  $\delta = 6.07/6.06$ ,  $5.80/5.78$ , and  $0.17/0.20$  ppm;  $^{13}\text{C}$  NMR:  $\delta = 116.6/115.6$ ,  $114.3/113.7$  and  $110.5/109.9$  ppm) in about 2:1 ratio, and  $^{171}\text{Yb}$  NMR spectrum also exhibited two broad singlets at  $356$  and  $177$  ppm. On the other hand, the borabenzene and boratabenzene rings, and the  $-\text{CH}_2\text{P}(\text{CH}_3)_2$  moiety exhibited only one set of signals in the  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR spectra. The above NMR observations clearly indicated that **3** existed as two conformation isomers in the presence of THF: one is the *syn* isomer with the  $-\text{SiMe}_3$  group and the pendant borabenzene ring at the same side, and the other is the *anti*-isomer with  $-\text{SiMe}_3$  group and the pendant boratabenzene ring at the opposite side (Scheme 3). The identification of the *syn* and *anti* isomers was accomplished with the aid of NOESY (Fig. 2) experiment. Therefore, the *syn* isomer was identified as the major species with an NOE interaction between the  $-\text{SiMe}_3$  group and the neutral

**Scheme 2.** The protonolysis reactions of **1** with 1-trimethylsilylcyclopentadiene and 1,3-bis(trimethylsilyl)cyclopentadiene.

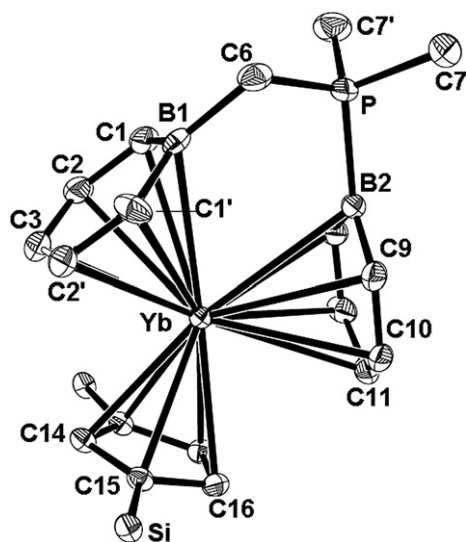
Scheme 3. Two isomers of **3** in THF.

boratabenzene ring. The  $^{13}\text{C}$  NMR signals of **3** in THF- $d_8$  at room temperature are somewhat broad, which became sharp when the temperature was raised up to 70 °C. The assignment of the  $^{13}\text{C}$  NMR signals for both *anti* and *syn* isomers are shown in Fig. 3.

Since the ligand redistribution process can not be completely inhibited by introducing the 1-trimethylsilylcyclopentadienyl ligand, the more bulky 1,3-bis(trimethylsilyl)cyclopentadiene was employed. The reaction was performed in benzene for 36 h and gave a deep green solution, from which the dark green divalent ytterbium (1,3-bis(trimethylsilyl)cyclopentadienyl)(boratabenzene) complex **4** was isolated in 95% yield (Scheme 2). **4** is readily soluble in benzene and only sparingly soluble in hexane. In contrast to **3**, single crystals

Fig. 2. NOESY spectrum of **3** in THF- $d_8$ .Fig. 3.  $^{13}\text{C}$  NMR spectra of **3** in THF- $d_8$  at room temperature (a) and 70 °C (b) ( $N_o$ : *ortho*-neutral boratabenzene;  $A_o$ : *ortho*-anionic boratabenzene).





**Fig. 4.** Molecular structure of **4** with thermal ellipsoids at the 30% probability level. Methyl groups of  $-\text{SiMe}_3$  and hydrogen atoms are omitted for clarity. Only one of two disordered components is shown.

of **4** can be obtained from a toluene–hexane mixture at  $-35\text{ }^\circ\text{C}$  without any ligand redistribution products. The  $^1\text{H}$  NMR spectrum of **4** in  $\text{C}_6\text{D}_6$  displayed well resolved signals for the borabenzene ( $\delta = 7.60, 6.88$  and  $6.52$  ppm) and boratabenzene rings ( $\delta = 7.50, 7.05$  and  $6.22$  ppm), and two doublets at  $1.41$  and  $0.79$  ppm for the  $-\text{CH}_2\text{P}(\text{CH}_3)_2$  moiety. The signals for the  $1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3$  ligand appear at  $6.64, 6.41$  and  $0.39$  ppm. The  $^{11}\text{B}$  NMR ( $\delta = 34.2$  and  $25.5$  ppm),  $^{31}\text{P}$  NMR ( $\delta = -17.4$  ppm) and  $^{171}\text{Yb}$  NMR ( $\delta = -196$  ppm) spectra of **4** in  $\text{C}_6\text{D}_6$  all showed broad signals.

Single crystals of **4** suitable for the X-ray diffraction studies were obtained from a toluene–hexane solution at  $-35\text{ }^\circ\text{C}$ . An ORTEP diagram is shown in Fig. 4, and the selected bond lengths are listed in Table 1. The anionic boratabenzene ring and the adjacent  $-\text{CH}_2\text{P}(\text{CH}_3)_2$  moiety are disordered between two positions with *sof*-s 0.5 and 0.5. The complex **4** exhibits a bent metallocene-type structure with the central divalent Yb ion coordinated by the anionic boratabenzene and  $1,3\text{-bis(trimethylsilyl)cyclopentadienyl}$  ligands, and the pendant neutral borabenzene ring lies in the front side of the metallocene wedge in a  $\eta^6$  coordination fashion. The anionic boratabenzene in **4** coordinated to the Yb ion in an intermediate  $\eta^3\text{--}\eta^6$  mode. (Yb–B1 =  $3.02\text{ \AA}$ , Yb–C1 =  $3.01\text{ \AA}$ , Yb–C2 =  $2.93\text{ \AA}$  vs. Yb–C3 =  $2.84\text{ \AA}$ , Yb–C1' =  $2.83\text{ \AA}$ , Yb–C2' =  $2.78\text{ \AA}$ ). The distances from Yb ion to the atoms on neutral borabenzene ring ( $3.04\text{ \AA}$  for B1,  $2.96\text{--}3.00\text{ \AA}$  for C9–C11) are significantly longer than those in **1** ( $2.87\text{--}2.89\text{ \AA}$ ), indicating that the interaction between Yb ion and neutral borabenzene in **4** is weaker than that in **1**. The average Yb–C (Cp) distance of  $2.76\text{ \AA}$  is longer than those of  $2.66\text{ \AA}$  reported for both solvent-free divalent complex  $[1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3]_2\text{Yb}$  [**12**] and  $[1,3\text{-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Yb}$  [**3b**].

As observed in **2a** and **3**,  $^1\text{H}$  NMR spectrum of **4** revealed upshift resonances of the neutral borabenzene ring ( $6.52, 7.60$  and  $6.88$  ppm for the *ortho*, *meta* and *para* protons, respectively) compared to those of  $\text{C}_5\text{H}_5\text{B} \leftarrow \text{PMe}_3$ . Addition of two drops of THF- $d_8$  to **4** in  $\text{C}_6\text{D}_6$  rapidly changed the solution color from green to red. The signals for the *ortho* and *meta* protons of neutral borabenzene shifted to the lower field ( $6.88$  and  $7.86$  ppm for the *ortho* and *meta* protons, respectively), and the signals for the *para* proton shifted to the higher field ( $6.69$  ppm). As that observed in **2a** and **3**, these datum again indicated the interaction between the neutral borabenzene and the ytterbium center in benzene, which is

interrupted in the presence of  $\sigma$ -donor solvent THF. The  $^1\text{H}$  NMR spectrum of **4** in neat THF- $d_8$  is close to those of **2a** and **3** in THF- $d_8$ : the signals at  $7.31, 7.18$  and  $6.44$  ppm for the neutral borabenzene, those at  $6.51, 6.76$  and  $6.47$  ppm for the anionic boratabenzene. The selected  $^1\text{H}$  NMR datum of **2a**, **3** and **4** in  $\text{C}_6\text{D}_6$  and THF- $d_8$  were listed in Table 2 for comparison.

### 3. Conclusion

The solvent-free divalent ytterbium bis(boratabenzene) complex  $[\text{C}_5\text{H}_5\text{BCH}_2(\text{CH}_3)_2\text{P} \rightarrow \text{BC}_5\text{H}_5]_2\text{Yb}$  (**2a**) and heteroleptic complexes  $[\text{C}_5\text{H}_3\text{R}^1\text{R}^2][\text{C}_5\text{H}_5\text{BCH}_2(\text{CH}_3)_2\text{P} \rightarrow \text{BC}_5\text{H}_5]\text{Yb}$  (**3**:  $\text{R}^1 = \text{SiMe}_3$ ,  $\text{R}^2 = \text{H}$ ; **4**:  $\text{R}^1 = \text{R}^2 = \text{SiMe}_3$ ) were synthesized and characterized. The protonolysis reaction of the solvent-free ansa-heteroborabenzene divalent lanthanide amide  $[\text{C}_5\text{H}_5\text{BCH}_2(\text{CH}_3)_2\text{P} \rightarrow \text{BC}_5\text{H}_5]\text{Yb N}(\text{SiMe}_3)_2$  (**1**) with cyclopentadiene gave **2**, while those with  $1\text{-trimethylsilylcyclopentadiene}$  and  $1,3\text{-bis(trimethylsilyl)cyclopentadiene}$  gave **3** and **4**, respectively. This provides a useful pathway to access to the solvent-free divalent ytterbium boratabenzene complexes. The complexes **2a**, **3** and **4** featured the interactions between the pendant neutral borabenzene and the ytterbium center both in the solid-state and in benzene, which can be easily interrupted by the addition of  $\sigma$ -donor solvent THF. This indicates that the coordinated neutral borabenzene in these complexes can function as a switch towards certain substrates, which may result in some interesting reactivities. The reactivities of these solvent-free divalent ytterbium boratabenzene complexes are under investigation.

### 4. Experimental

#### 4.1. General experimental details

All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a nitrogen filled glovebox. Benzene, hexane,  $\text{C}_6\text{D}_6$ , and THF- $d_8$  were dried over Na/K alloy, followed by vacuum transfer, and stored in the glovebox. **1** was prepared as we previously reported [8c].  $1\text{-trimethylsilylcyclopentadiene}$  [13] and  $1,3\text{-bis(trimethylsilyl)cyclopentadiene}$  [14] were synthesized according to the literature procedures.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded on a VARIAN 400 MHz spectrometer at  $400\text{ MHz}$ ,  $100\text{ MHz}$  and  $160\text{ MHz}$ , respectively.  $^{11}\text{B}$  NMR and  $^{171}\text{Yb}$  NMR spectra were recorded on a Bruker DXP 400 MHz spectrometer at  $128\text{ MHz}$  and  $70\text{ MHz}$ . All chemical shifts were reported in  $\delta$  units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, to external  $\text{BF}_3 \cdot \text{OEt}_2$  and  $\text{H}_3\text{PO}_4$  for boron and phosphorous chemical shifts, and to  $0.171\text{ M } [\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{THF})_2]$  in THF [ $\delta$  ( $^{171}\text{Yb}$ ) =  $0$  ppm for  $\Xi$  ( $^{171}\text{Yb}$ ) =  $17.499306\text{ MHz}$ ] for ytterbium chemical shifts. Elemental analysis was performed by Analytical Laboratory of Shanghai Institute of Organic Chemistry.

#### 4.2. Synthesis of **2a**

**1** ( $75\text{ mg}$ ,  $0.134\text{ mmol}$ ) and the freshly distilled cyclopentadiene ( $10\text{ mg}$ ,  $0.150\text{ mmol}$ ) were mixed in  $2\text{ mL}$  of benzene. The reaction mixture was standing at room temperature for 7 days. The color of the reaction solution turned from dark blue to pale green, and black blocks of **2a** and a yellow crystalline solid of **2b** precipitated from the solution. The black blocks of **2a** were carefully separated from the slurry of **2b**, washed with benzene and hexane, and dried under vacuum ( $35\text{ mg}$ ,  $84\%$  yield). **2b** was isolated by centrifugation of the slurry, washed with benzene and hexane, and dried under vacuum ( $17\text{ mg}$ ,  $84\%$  yield).  $^1\text{H}$  NMR ( $400\text{ MHz}$ ,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta = 7.90$  (m, 2H; PBCHCHCH),  $7.33$  (t,  $^3J_{\text{H-H}} = 7.4\text{ Hz}$ , 1H; PBCHCHCH),  $7.07$  (t,  $^3J_{\text{H-H}} = 8.2\text{ Hz}$ , 2H; CBCHCHCH),  $6.73$  (t,  $^3J_{\text{H-H}} = 8.8\text{ Hz}$ , 2H;

PBCHCHCH), 6.57 (d,  $^3J_{\text{H-H}} = 10.4$  Hz, 2H; CBCHCHCH), 6.03 (dt,  $^3J_{\text{H-H}} = 7.4$  Hz,  $^4J_{\text{H-H}} = 1.2$  Hz, 1H; CBCHCHCH), 1.49 (d,  $^2J_{\text{P-H}} = 17.2$  Hz, 2H;  $\text{P}(\text{CH}_3)_2$ ), 0.99 (d,  $^3J_{\text{P-H}} = 10.8$  Hz, 6H;  $\text{P}(\text{CH}_3)_2$ );  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25 °C): 7.21 (m, 2H, PBCHCHCH), 7.17 (t,  $^3J_{\text{H-H}} = 8.4$  Hz, 2H; PBCHCHCH), 6.81 (t,  $^3J_{\text{H-H}} = 9.0$  Hz, 2H; CBCHCHCH), 6.51 (t, 1H; PBCHCHCH, overlapped), 6.50 (d,  $^3J_{\text{H-H}} = 8.8$  Hz, 2H; CBCHCHCH), 6.31 (t,  $^3J_{\text{H-H}} = 6.2$  Hz, 1H; CBCHCHCH), 1.83 (d,  $^2J_{\text{P-H}} = 15.6$  Hz, 2H;  $\text{P}(\text{CH}_3)_2$ ), 1.36 (d,  $^3J_{\text{P-H}} = 11.2$  Hz, 6H;  $\text{P}(\text{CH}_3)_2$ );  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ , 25 °C):  $\delta = 135.1, 133.2$  (d,  $^2J_{\text{P-C}} = 17.1$  Hz), 130.2, 129.0 (br), 118.9, 112.2 (Borabenzene-C), 17.3 (br d,  $^1J_{\text{P-C}} = 29.7$  Hz,  $\text{P}(\text{CH}_3)_2$ ), 11.1 (d,  $^1J_{\text{P-C}} = 42.3$  Hz,  $\text{P}(\text{CH}_3)_2$ );  $^{31}\text{P}$  NMR (160 MHz, THF- $d_8$ , 25 °C):  $\delta = -12.6$  (d,  $^1J_{\text{B-P}} = 127.8$  Hz);  $^{11}\text{B}$  NMR (128 MHz, THF- $d_8$ , 25 °C):  $\delta = 34.0$  (br s, CB), 23.9 (br d,  $^1J_{\text{B-P}} = 99.3$  Hz, PB);  $^{171}\text{Yb}$  NMR (70 MHz, THF- $d_8$ , 25 °C)  $\delta = 142$  (br s); Anal. Calcd for  $\text{C}_{26}\text{H}_{36}\text{B}_4\text{P}_2\text{Yb}$ : C, 49.82; H, 5.79. Found: C, 49.95; H, 5.79. **2b**:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = 6.15$  (s)

#### 4.3. Synthesis of **3**

**1** (80 mg, 0.143 mmol) and 1-trimethylsilylcyclopentadiene (24 mg, 0.173 mmol) were mixed in 4 mL of benzene. The reaction mixture was standing at room temperature for 2 days. The color of the reaction solution turned from dark blue to dark green. The solvent was then removed under vacuum, the resulted green solid was washed with hexane, and dried under vacuum (64 mg, 84% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = 7.53$  (br s, 2H; PBCHCHCH), 7.41 (br s, 2H; CBCHCHCH), 6.97 (br s, 1H; CBCHCHCH), 6.78 (br s, 1H; PBCHCHCH), 6.49 (br s, 2H; CBCHCHCH), 6.36 (t, 2H;  $\text{Me}_3\text{SiCCHCH}$ ), 6.20 (t, 2H;  $\text{Me}_3\text{SiCCHCH}$ ), 6.18 (br s, 2H; PBCHCHCH), 1.41 (d,  $^2J_{\text{P-H}} = 16.8$  Hz, 2H;  $\text{P}(\text{CH}_3)_2$ ), 0.79 (d,  $^2J_{\text{P-H}} = 10.0$  Hz, 6H;  $\text{P}(\text{CH}_3)_2$ ), 0.39 (s, 9H;  $\text{Si}(\text{CH}_3)_3$ );  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25 °C):  $\delta = 7.20$  (br s, 4H, PBCHCHCH and PBCHCHCH), 6.82 (t,  $^3J_{\text{H-H}} = 9.0$  Hz, 2H; CBCHCHCH), 6.50 (d,  $^3J_{\text{H-H}} = 8.4$  Hz, 2H; CBCHCHCH), 6.51 (t, 1H; CBCHCHCH), 6.32 (br s, 1H; PBCHCHCH), 6.07 and 6.06 (t, 2H;  $\text{Me}_3\text{SiCCHCH}$ ), 5.80 and 5.78 (t, 2H;  $\text{Me}_3\text{SiCCHCH}$ ), 1.83 (d,  $^2J_{\text{P-H}} = 15.2$  Hz, 2H;  $\text{P}(\text{CH}_3)_2$ ), 1.35 (d,  $^2J_{\text{P-H}} = 11.2$  Hz, 6H;  $\text{P}(\text{CH}_3)_2$ ), 0.20 and 0.17 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ );  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 70 °C): 7.21 (m, 4H, PBCHCHCH and PBCHCHCH), 6.79 (t,  $^3J_{\text{H-H}} = 9.0$  Hz, 2H; CBCHCHCH), 6.51 (t,  $^3J_{\text{H-H}} = 6.8$  Hz, 1H; CBCHCHCH), 6.48 (d,  $^3J_{\text{H-H}} = 10.8$  Hz, 2H; CBCHCHCH), 6.29 (br s, 1H; PBCHCHCH), 6.07 (s, 2H,  $\text{Me}_3\text{SiCCHCH}$ ), 5.80 (s, 2H,  $\text{Me}_3\text{SiCCHCH}$ ), 1.82 (d,  $^2J_{\text{P-H}} = 15.2$  Hz, 2H;  $\text{P}(\text{CH}_3)_2$ ), 1.38 (d,  $^2J_{\text{P-H}} = 11.6$  Hz, 6H;  $\text{P}(\text{CH}_3)_2$ ), 0.19 and 0.18 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ , 25 °C):  $\delta = 134.7, 133.2$  (d,  $^2J_{\text{P-C}} = 17.3$  Hz), 129.4 (br), 128.4 (br), 118.8, 116.6, 115.6, 114.3, 113.7, 111.5, 110.5, 109.9 (Borabenzene-C and Cp-C), 17.3 (br d,  $^1J_{\text{P-C}} = 29.7$  Hz,  $\text{P}(\text{CH}_3)_2$ ), 11.1 (d,  $^1J_{\text{P-C}} = 42.7$  Hz,  $\text{P}(\text{CH}_3)_2$ ), 1.3 and 1.2 ( $\text{Si}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ , 70 °C):  $\delta = 135.0, 133.6$  (d,  $^2J_{\text{P-C}} = 16.3$  Hz), 129.7 (br), 128.3 (br), 119.0, 116.9, 115.8, 114.9, 111.8, 110.7, 110.0 (Borabenzene-C and Cp-C), 17.3 (br,  $\text{P}(\text{CH}_3)_2$ ), 11.1 (d,  $^1J_{\text{P-C}} = 42.4$  Hz,  $\text{P}(\text{CH}_3)_2$ ), 1.2 ( $\text{Si}(\text{CH}_3)_3$ );  $^{31}\text{P}$  NMR (160 MHz, THF- $d_8$ , 25 °C):  $\delta = -12.7$  (d,  $^1J_{\text{B-P}} = 116.5$  Hz);  $^{11}\text{B}$  NMR (128 MHz, THF- $d_8$ , 25 °C):  $\delta = 33.7$  (br s, CB), 23.9 (br d,  $^1J_{\text{B-P}} = 104.4$  Hz, PB);  $^{171}\text{Yb}$  NMR (70 MHz, THF- $d_8$ , 25 °C)  $\delta = 356$  (br s) and 177 (br s); Anal. Calcd for  $\text{C}_{21}\text{H}_{31}\text{B}_2\text{PSiYb}$ : C, 46.95; H, 5.82. Found: C, 46.71; H, 6.48.

#### 4.4. Synthesis of **4**

**1** (80 mg, 0.143 mmol) and 1,3-bis(trimethylsilyl)cyclopentadiene (33 mg, 0.157 mmol) were mixed in 5 mL of benzene. The reaction mixture was standing at room temperature for 36 h. The color of the reaction solution turned from dark blue to dark green. Removal of the solvent under vacuum gave a dark green solid. (83 mg, 95% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = 7.60$  (m, 2H, PBCHCHCH), 7.50 (t,

$^3J_{\text{H-H}} = 8.4$  Hz, 2H; CBCHCHCH), 7.05 (t,  $^3J_{\text{H-H}} = 6.6$  Hz, 1H; CBCHCHCH), 6.88 (t,  $^3J_{\text{H-H}} = 6.0$  Hz, 1H; PBCHCHCH), 6.64 (s, 1H,  $\text{Me}_3\text{SiCCHCHSiMe}_3$ ), 6.52 (t,  $^3J_{\text{H-H}} = 8.6$  Hz, 2H; PBCHCHCH), 6.41 (d,  $^4J_{\text{H-H}} = 1.6$  Hz, 2H;  $\text{Me}_3\text{SiCCHCHCHSiMe}_3$ ), 6.22 (d,  $^3J_{\text{H-H}} = 10.0$  Hz, 2H; CBCHCHCH), 1.41 (d,  $^2J_{\text{P-H}} = 16.8$  Hz, 2H;  $\text{P}(\text{CH}_3)_2$ ), 0.79 (d,  $^2J_{\text{P-H}} = 11.6$  Hz, 6H;  $\text{P}(\text{CH}_3)_2$ ), 0.39 (s, 18H;  $\text{Si}(\text{CH}_3)_3$ );  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25 °C):  $\delta = 7.31$  (dd,  $^3J_{\text{H-H}} = 8.2$  Hz,  $^4J_{\text{H-H}} = 2.0$  Hz, 2H; PBCHCHCH), 7.18 (m, 2H; PBCHCHCH), 6.76 (t,  $^3J_{\text{H-H}} = 9.4$  Hz, 2H; CBCHCHCH), 6.53 and 6.52 (two doublets,  $^4J_{\text{H-H}} = 2.0$  Hz, 1H;  $\text{Me}_3\text{SiCCHCHSiMe}_3$ ), 6.51 (d,  $^3J_{\text{H-H}} = 8.8$  Hz, 2H; CBCHCHCH), 6.47 (t,  $^3J_{\text{H-H}} = 8.0$  Hz, 1H; CBCHCHCH), 6.44 (t,  $^3J_{\text{H-H}} = 7.2$  Hz, 1H; PBCHCHCH), 6.09 and 6.08 (two doublets,  $^4J_{\text{H-H}} = 2.0$  Hz, 2H;  $\text{Me}_3\text{SiCCHCHCHSiMe}_3$ ), 1.77 (d,  $^2J_{\text{P-H}} = 15.2$  Hz, 2H;  $\text{P}(\text{CH}_3)_2$ ), 1.31 (d,  $^2J_{\text{P-H}} = 11.2$  Hz, 6H;  $\text{P}(\text{CH}_3)_2$ ), 0.19 (two singlets, 18H,  $\text{Si}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = 135.1$  (d,  $^2J_{\text{P-C}} = 14.3$  Hz), 134.4, 128.5, 127.6, 121.8, 121.5, 118.0, 115.7 (Borabenzene-C and Cp-C), 14.4 (br d,  $^1J_{\text{P-C}} = 25.7$  Hz,  $\text{P}(\text{CH}_3)_2$ ), 10.3 (d,  $^1J_{\text{P-C}} = 40.6$  Hz,  $\text{P}(\text{CH}_3)_2$ ), 0.7 ( $\text{Si}(\text{CH}_3)_3$ );  $^{31}\text{P}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = -17.4$  (br);  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = 34.2$  (br s, CB), 25.5 (br s, PB);  $^{171}\text{Yb}$  NMR (70 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  $\delta = -196$  (br s); Anal. Calcd for  $\text{C}_{24}\text{H}_{39}\text{B}_2\text{PSi}_2\text{Yb}$ : C, 47.30; H, 6.45. Found: C, 47.26; H, 6.07.

#### 4.5. X-ray crystallography

Suitable single crystals of **2a** and **4** were sealed in thin-walled glass capillaries, data collection of **2a** was performed at 20(2) °C on a Bruker SMART diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). For **4**, data collection was performed at -100(2) °C on a Bruker SMART APEXII diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SADABS.

**Table 3**  
Crystallographic data of **2a** and **4**.

Empirical formula	$\text{C}_{26}\text{H}_{36}\text{B}_4\text{P}_2\text{Yb}$	$\text{C}_{24}\text{H}_{39}\text{B}_2\text{PSi}_2\text{Yb}$
Formula weight	626.77	609.36
Temperature (K)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbcn	Pnma
a (Å)	10.3614(10)	13.4464(6)
b (Å)	12.9259(13)	16.8641(8)
c (Å)	20.501(2)	12.1669(6)
Volume (Å <sup>3</sup> )	2745.8(5)	2759.0(2)
Z	4	4
Dcalc (mg/m <sup>3</sup> )	1.516	1.467
Absorption coefficient (mm <sup>-1</sup> )	3.535	3.544
F(000)	1248	1224
Crystal size (mm <sup>3</sup> )	0.235 × 0.221 × 0.087	0.294 × 0.251 × 0.233
$\theta$ Range for data collection (°)	1.99–27.49	2.06–28.33
Completeness to $\theta = 27.49$ (%)	99.7	98.8
Reflections collected	15618	35205
Independent reflections [R <sub>int</sub> ]	3148 [0.1235]	3508 [0.0276]
Absorption correction	empirical	empirical
Maximum and minimum transmission	1.0000; 0.6449	0.4988; 0.4305
Data/restraints/parameters	15618/0/152	35205/4/184
Final R indices (I > 2 $\sigma$ (I))	R <sub>1</sub> = 0.0392 wR <sub>1</sub> = 0.0896	R <sub>1</sub> = 0.0281 wR <sub>1</sub> = 0.0749
R indices (all data)	R <sub>2</sub> = 0.0681 wR <sub>2</sub> = 0.0988	R <sub>2</sub> = 0.0353 wR <sub>2</sub> = 0.0834
Goodness-of-fit on F <sup>2</sup>	0.903	1.023
Largest difference peak and hole (eÅ <sup>-3</sup> )	2.062 and -0.996	3.811 and -1.481

The structures were solved by direct methods and refined on  $F^2$  by full-matrix least squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXL-97 program [15–19]. The software used is listed in the references, crystallographic data and refinement for **2a** and **4** are listed in Table 3.

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