

## Note

## Synthesis of a transition-metalated phosphinoborane dimer

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## Abstract

The unprecedented aggregate of a transition-metalated phosphinoborane was reported.  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{BCl}_3)\text{HPh}\}$  was treated with *n*-BuLi to yield the iron-phosphinoborane dimer,  $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\mu\text{-BCl}_2)\text{Ph}\}]_2$ , via a dehydrohalogenation reaction. The X-ray structural study revealed that the dimer has a bent  $\text{P}_2\text{B}_2$  4-membered ring with two iron complex fragments in equatorial positions. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Phosphinoborane; Iron; Aggregation; Dimer; X-ray structure; Dehydrohalogenation

## 1. Introduction

The chemistry of transition-metal complexes with phosphorus ligands has been developed for decades to be an important part of the current inorganometallic chemistry. The phosphide complexes, i.e., metalated phosphines ( $\text{L}_n\text{M-PR}_2$ ), are the simplest compounds with a metal–phosphorus covalent bond, and their borane adducts ( $\text{L}_n\text{M-P}(\text{BR}_3)\text{R}_2$ ) have been also known to date [1]. The interests in the borane adducts of the transition-metalated phosphorus compounds emerge, in part, from their isoelectronic relationship to the transition-metalated carbon compounds. One of the most notable differences between the P–B and the C–C compounds is that the P–B compounds isoelectronic to alkenes or alkynes have greater tendency to aggregate in a head-to-tail fashion (Chart 1) [2–7]. Depending on the preparative conditions adopted and on substituents on both the phosphorus and the boron atoms, the resulting compounds vary from dimers to polymers in a cyclic or linear form. The condensed P–B compounds have attracted significant attention for several decades as possible candidates for high-performance inorganic materials [8]. In this regard, the study on the conden-

sation reaction of the transition-metalated P–B compounds is of considerable interest in the development of the transition-metal-containing inorganic macromolecules, having attractive and new physical and chemical properties [9].

Paine and his co-workers reported some transition-metalated compounds of **II** in Chart 1, such as a cyclic trimer with an M–P dative bond [10], and cyclic dimers with an M–P covalent [11] or an M–P dative [10,12] bond, in which the transition-metal fragments were introduced to the P–B frameworks after aggregation. However, there is so far no example of the transition-metalated derivatives of aggregated compounds **I**, though the chemistry of the non-metalated compounds **I** started earlier than that of the **II**. We here report the first synthesis of the transition-metalated phosphinoborane dimer (**I**) by the aggregation of transition-metalated P–B monomers.

## 2. Results and discussion

The borane adduct of an iron-phosphide complex,  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{BCl}_3)\text{HPh}\}$  **1** was treated with *n*-BuLi in toluene to yield a yellow powder. The X-ray crystallographic study (vide infra) revealed that the product is a novel iron-phosphinoborane dimer,  $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\mu\text{-BCl}_2)\text{Ph}\}]_2$  **2** (50% yield, Scheme 1). The resulting

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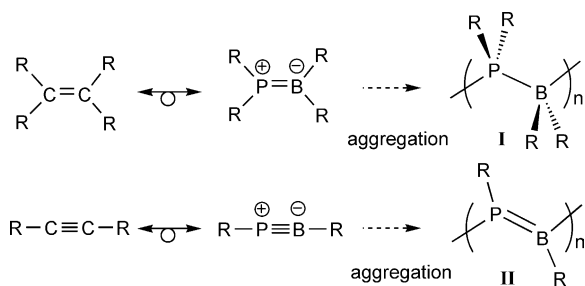
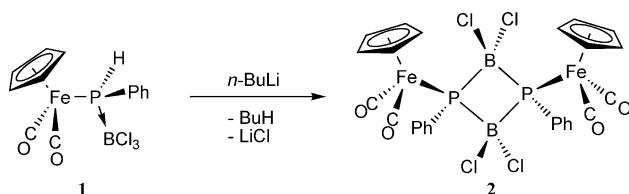


Chart 1.



Scheme 1.

product can be handled under air for a short period but decomposes slowly. This reaction would be initiated by the P–H proton abstraction in **1** by *n*-BuLi with a chloride anion concomitantly released to give a phosphinoborane monomer as a transient species [13]. The monomer promptly aggregated with another monomer to form a dimer with a P<sub>2</sub>B<sub>2</sub> 4-membered ring. In the similar dehydrohalogenation reactions of non-metallated phosphine–borane adducts, NEt<sub>3</sub> is often used as a base [5,7]. However in the case of **1**, a much stronger base, i.e., *n*-BuLi was needed to eliminate the P–H proton, because of the lower acidity of the proton in **1**, indicating the great electron donation from the iron complex fragment toward the phosphorus.

Paine and coworkers [14] reported a phosphinoborane with a zirconocene fragment, Cp<sub>2</sub>Zr[P(H)B{N<sup>i</sup>Pr<sub>2</sub>}{N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub>, which was prepared by the reaction of Cp<sub>2</sub>ZrCl<sub>2</sub> with LiP(H)B{N<sup>i</sup>Pr<sub>2</sub>}{N(SiMe<sub>3</sub>)<sub>2</sub>} and can be obtained as a monomer. In this complex, the boron and nitrogen atoms have both trigonal planar geometries, apparently demonstrating the strong π interaction between the boron and the nitrogen atoms. This π interaction, probably together with steric shielding by the bulky amino groups, should decrease the acceptor ability of the boron atom, and thus discourage the intermolecular aggregation [5]. In contrast, the electron-withdrawing and sterically less-demanding chloride atoms on the boron in **2** would encourage the intermolecular, rather than intramolecular, acid–base interaction between the boron and phosphorus atoms to form the dimer.

The IR spectrum of **2** shows two absorption bands at 1989 and 2040 cm<sup>-1</sup> attributed to the terminal carbonyl stretchings, and they are lower in wave number than those of the starting complex **1** (2005 and 2050 cm<sup>-1</sup>).

This indicates that the electron density on the iron atom is higher in **2** to encourage the Fe–CO back donation. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, **2** resonates at –10.75 ppm which is at a higher magnetic field than **1** (–0.82 ppm). The signal of **2** is very broad and the B–P coupling cannot be identified, whereas the <sup>11</sup>B NMR spectrum shows a broad triplet at 4.55 ppm with *J*<sub>BP</sub> = 79 Hz, which is comparable in magnitude to those for [(Me<sub>3</sub>Si)<sub>2</sub>PBCl<sub>2</sub>] (*J*<sub>BP</sub> = 77 Hz) [15] and [Et<sub>2</sub>PBCl<sub>2</sub>]<sub>2</sub> (*J*<sub>BP</sub> = 100 Hz) [16]. It was reported that the NMR spectra of [Me<sub>2</sub>BP(*t*-Bu)<sub>2</sub>]<sub>2</sub> are temperature- and concentration-dependent owing to the equilibrium between the dimer and monomers [17]. However, variable temperature NMR measurements of **2** did not provide any evidence for such an equilibrium up to 70 °C. The <sup>11</sup>B NMR chemical shift of **2** is indicative of the tetracoordination around the boron atom even at elevated temperatures, revealing that the dimeric structure of **2** is persistently retained in solution.

The ORTEP drawing of **2** is given in Fig. 1 with selected bond distances and angles. The resulting dimer has an unexpected *cis* configuration in contrasted to the related type-II compound, [(*t*-Bu){Cr(CO)<sub>5</sub>}PB(NEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> which has a *trans* configuration [12b]. Although the <sup>31</sup>P NMR spectrum of the reaction mixture showed a few additional weak signals, which could be attributed to the *trans* isomer of **2** and/or to higher aggregates, we could not identify any of them because of their small quantities. Heating **2** in toluene led to slow decomposition, and no evidence for either *cis/trans* isomerization or farther rearrangements (e.g., dissociation of the dimer or higher aggregation of the monomer units) was observed. To date, fifteen compounds having the similar P<sub>2</sub>B<sub>2</sub> ring were structurally characterized [15,17–27], and the average distance of the P–B bonds in **2** (1.998 Å) is relatively short compared with the range (1.989–2.082 Å), indicating the stronger P–B bond in **2**. The P<sub>2</sub>B<sub>2</sub> ring in

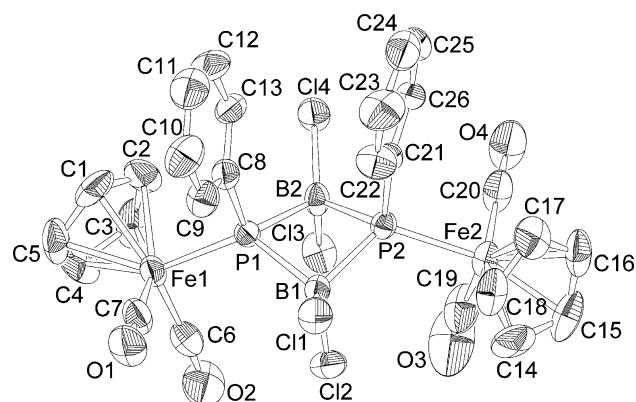


Fig. 1. ORTEP drawing of **2** showing a numbering scheme. Selected bond distances (Å) and angles (deg): Fe(1)–P(1) 2.270(3), Fe(2)–P(2) 2.262(3), P(1)–B(1) 1.988(9), P(1)–B(2) 2.016(8), P(2)–B(1) 1.996(9), P(2)–B(2) 1.992(9); B(1)–P(1)–B(2) 85.1(4), B(1)–P(2)–B(2) 85.5(4), P(1)–B(1)–P(2) 89.7(4), P(1)–B(2)–P(2) 89.0(3).

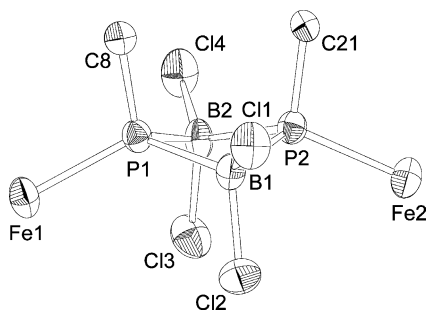


Fig. 2. Core structure of the  $P_2B_2$  ring in **2**.

**2** is non-planar (Fig. 2), although the planar conformation is rather common in the above examples. The only two compounds [18,24] were reported to have a bent  $P_2B_2$  ring without a structural constraint by a chelate, which leads to the bent structure by force [25,27]. The dihedral angle in **2** defined by the P1–B1–B2–P2 sequence is  $34.1^\circ$  and that defined by the B1–P1–P2–B2 sequence is  $35.3^\circ$ , and these values are larger than those of the two above examples. Although the  $P_2B_2$  ring in **2** has a *cis* configuration, the bulky iron complex fragments are in the equatorial positions of the bent  $P_2B_2$  ring and they are far each other enough to avoid the steric repulsion between them and/or with Cl atoms on the boron atoms. In contrast, the two bulky *t*-Bu groups in [*t*-Bu(H)PBPh<sub>2</sub>]<sub>2</sub> are in *trans* positions on the planar  $P_2B_2$  ring [21] as are the transition-metal fragments in [(*t*-Bu){Cr(CO)<sub>5</sub>}PB(NEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub>. [12b] It seems that such *cis/trans* and planar/bent preferences of the rings would be subjected to a subtle balance of both steric and electronic factors of the substituents.

In order to obtain the transition-metal-coordinated macromolecules, two procedures can be conceivable: one is the introduction of transition-metal fragments onto the macromolecular chain, and the other is the aggregation of transition-metalated monomers. In the former strategy, complete metalation of all monomer units would be more difficult as the chain becomes longer. This work reveals the possibility of the latter approach to the condensation of the transition-metalated phosphinoboranes.

### 3. Experimental

**Preparation of 2:** To a toluene solution (80 mL) of **1** [28] (0.950 g, 2.36 mmol) was added a 1.56 M hexane solution 2.10 mL of *n*-BuLi (3.28 mmol) at  $-78^\circ\text{C}$ . After overnight stirring, the mixture was dried under reduced pressure and then the residue was charged on a silica gel column with toluene as a solvent under air. Checking the IR spectrum of the effluent, a yellow band eluted with toluene/hexane = 3/1 was collected and the volatile components were removed under reduced pressure to

give a bright yellow powder of **2** (0.432 g, 0.589 mmol, 50% yield). When the product has dark yellow color, the purification by a short silica gel column with ether as an eluent is needed to eliminate remaining impurities. Anal. Calc. for  $C_{26}H_{20}B_2Cl_4Fe_2O_4P_2$ : C, 42.57; H, 2.75. Found: C, 42.43; H, 2.78. IR ( $\nu_{CO}$ , in toluene): 1989, 2040  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$ , in  $C_6D_6$ ): 4.07 (s, 10H,  $C_5H_5$ ), 6.97–8.32 (m, 10H,  $C_6H_5$ ).  $^{31}\text{P}$  NMR ( $\delta$ , in  $C_6D_6$ ):  $-10.75$  (br).  $^{11}\text{B}$  NMR ( $\delta$ , in  $C_6D_6$ ): 4.55 (t,  $J_{BP} = 79.4$  Hz).  $^{13}\text{C}$  NMR ( $\delta$ , in  $C_6D_6$ ): 85.65 ( $C_5H_5$ ), 127.28 (t,  $J_{CP} = 4.0$  Hz, Ph), 134.95 (t,  $J_{CP} = 2.5$  Hz, Ph), 140.01 (t,  $J_{CP} = 6.2$  Hz, Ph), 212.42 (t,  $J_{CP} = 9.9$  Hz, CO).

**Crystal data for 2:**  $C_{26}H_{20}B_2Cl_4Fe_2O_4P_2$ , yellow, plate,  $0.30 \times 0.20 \times 0.10$  mm, monoclinic,  $P2_1$ ,  $a = 10.879(4)$  Å,  $b = 12.089(4)$  Å,  $c = 14.240(7)$  Å,  $\beta = 104.514(2)^\circ$ ,  $Z = 2$ . Data were collected on a Mac Science DIP2030 diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 200 K to a maximum  $2\theta$  of  $55.9^\circ$ . A total of 4317 reflections were collected. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and included at the final stage of refinements with fixed parameters. The solution and refinement of the structure gave  $R = 0.062$  and  $R_w = 0.105$  with  $GOF = 1.20$  for 3701 reflections regarded as observed ( $F_o > 3\sigma(F_o)$ ) and for 363 parameters.

### 4. Supplementary material

Crystallographic data for the complex **2** has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 233351 in CIF format. 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](mailto:deposit@ccdc.cam.ac.uk) or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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- [28] **1** was prepared by the borane-exchange reaction in benzene using  $\text{BCl}_3$  and  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{BH}_3)\text{Ph}\}$  which had been obtained from the reaction of  $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PH}_2\text{Ph}\}]\text{PF}_6$  with  $\text{NaBH}_4$  in THF. Anal. Calc. for  $\text{C}_{13}\text{H}_{11}\text{BCl}_3\text{FeO}_2\text{P}$ : C, 38.72; H, 2.75. Found: C, 39.10; H, 2.63. IR ( $\nu_{\text{CO}}$ , in  $\text{CH}_2\text{Cl}_2$ ): 2005, 2050  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$ , in  $\text{CDCl}_3$ ): 5.31 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.19 (d,  $J_{\text{HP}} = 348$  Hz, 1H, PH), 7.42–7.65 (m, 5H,  $\text{C}_6\text{H}_5$ ).  $^{31}\text{P}$  NMR ( $\delta$ , in  $\text{CH}_2\text{Cl}_2$ ): -0.82 (d, qua.,  $J_{\text{PH}} = 348$  Hz,  $J_{\text{PB}} = 132$  Hz).  $^{11}\text{B}$  NMR ( $\delta$ , in  $\text{CH}_2\text{Cl}_2$ ): 6.96 (d,  $J_{\text{BP}} = 130$  Hz).