

Syntheses of PBP Pincer Iridium Complexes: A Supporting Boryl Ligand

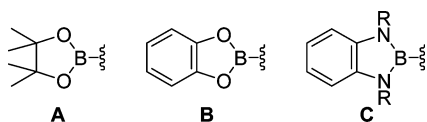
Yasutomo Segawa, Makoto Yamashita,* and Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo 7-3-1, Hongo, Bunkyo-ku, 113-8656 Tokyo, Japan

Received May 7, 2009; E-mail: makotoy@chembio.t.u-tokyo.ac.jp; nozaki@chembio.t.u-tokyo.ac.jp

Transition metal boryl complexes,¹ which have an anionic sp² boron ligand on the metal center, have been widely synthesized and applied to catalytic borylation reactions.² In all of these reactions, boryl ligands act as “reactive” ligands. It is known that the boryl ligand has a greater σ -donor ability than other monoanionic ligands of *p*-block elements in the second row of the periodic table, such as C, N, and O.³ If the boryl ligand is stabilized and acts as a “supporting” ligand, the strong electron-releasing property of the boryl ligand can be applied to functionalization reactions other than borylations.

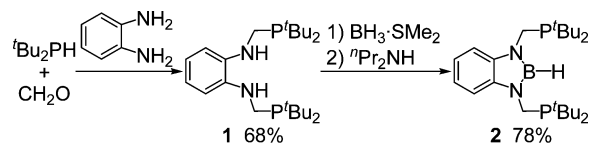
To stabilize highly reactive anionic ligands on metal centers, multidentate ligands are generally utilized to take advantage of the chelate effect. Among them, meridional tridentate pincer ligands can afford remarkable thermodynamic stability to metal complexes.⁴ Recent development of bulky and electron-rich phosphine-based PCP pincer ligands has resulted in high catalytic activities of their metal complexes in the transfer or acceptorless dehydrogenation of alkanes, where the rate-determining C–H activation step is accelerated by the high σ -donation of stabilized aryl ligands.⁵ However, there have been no attempts to prepare tridentate boryl ligand precursors even though transition metal complexes possessing a bidentate boryl ligand have been reported.⁶ The divalency of oxygen atoms in common boryl groups such as **A** (Bpin) or **B** (Bcat) may have led to the rarity of a multidentate boryl ligand because it is difficult to construct complex structures using divalent oxygen atoms. The use of trivalent nitrogen atoms enables the boryl group to possess branches (e.g., **C**), which can have various substituents containing heteroatoms for construction of multidentate ligands. In addition, nitrogen-based boryl ligands have a higher σ -donation ability than oxygen-based ones.⁷



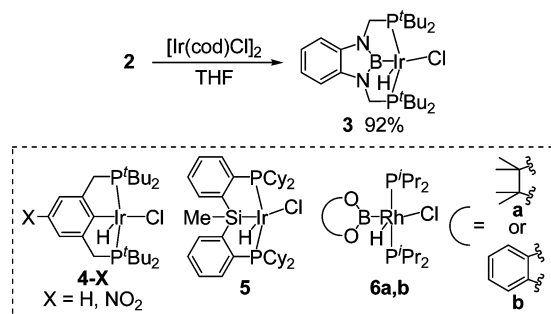
Herein, we report the synthesis of PBP iridium(III) complex **3** using newly prepared hydroborane precursor **2**, an evaluation of the σ -donor ability of the PBP ligand in carbonyl complex **4** compared to PCP ligands, and the synthesis of an iridium(I) ethylene complex.

The synthetic route to ligand precursor **2** is shown in Scheme 1. Compound **2** can be synthesized on a gram scale from commercially available precursors. Reaction of a mixture of di-*tert*-butylphosphine and paraformaldehyde with *o*-phenylenediamine gave 1,2-bis(di-*tert*-butylphosphinomethyl-amino)benzene **1** in 68% yield.⁸ Treatment of **1** with 3.3 equiv of BH₃·SMe₂ followed by the deprotection of the phosphine-borane using *n*-Pr₂NH gave hydroborane **2** in 78% yield. The B–H proton signal of **2** was observed at 5.36 ppm in its ¹H(¹¹B) NMR spectrum, and neither inter- nor intramolecular P–B interaction was observed in the solid state structure of **2**.

In the reaction of **2** with [Ir(cod)Cl]₂, B–H oxidative addition took place very smoothly to generate coordinatively unsaturated [PBP](hydrido)chloroiridium complex **3** in 92% yield (Scheme 2). The ³¹P NMR

Scheme 1. Synthesis of Hydroborane **2**

chemical shift of the phosphorus atom shifted from 17.0 ppm (**2**) to 85.9 ppm (**3**) indicating the complexation of the PBP ligand with iridium. The ¹¹B NMR signal shifted from 26.4 ppm (**2**) to 34.6 ppm (**3**) ppm, which indicates the existence of a B–Ir bond.⁹ The hydride ligand was detected by ¹H NMR (–29.27 ppm, t, ²J_{PH} = 13 Hz) and IR (ν_{IrH} = 2281 cm^{–1}) spectroscopies.

Scheme 2. Synthesis of PBP Iridium Complex **3** and Related Compounds **4**–**6**

Single crystals of **3** were obtained from its THF/hexane solution. As shown in Figure 1, the PBP ligand coordinates to the iridium center in a meridional fashion. This is the first example of a transition metal complex having a tridentate boryl ligand. In the structure of **3**, the central iridium atom formed a distorted trigonal bipyramidal structure, consisting of two apical phosphine ligands and equatorial hydride, boryl, and chloride ligands. The Ir–B length of 1.971(6) Å was slightly shorter than those of previously reported boryliridium complexes.^{1f} The P–Ir–P angle of 158.12(5)° was around the lower end of the range of those observed in the 16-electron benzene-based PCP iridium(III) system.^{5c,10} Narrow P–Ir–P angles have also been found in ferrocene-based PCP iridium complexes.⁵ⁿ The sum of the three angles around the boron atom, not including the hydride, is 359.8°, indicating sp² hybridization of the boron center. The bent B–Ir–Cl angle (157.67(17)°) is different from the linear C–Ir–Cl angle (179.33(14)°) in **4-NO₂**,¹¹ which is a corresponding PCP derivative with the same combination of the other ligands. Silyl pincer complex **5** was also reported to have a bent Si–Ir–Cl angle (130.64(5)°),¹² where an interaction between the silicon atom and hydride was suggested according to the shorter Si–H distance relative to the sum of van der Waals radii, but no Si–H coupling was observed by NMR spectroscopy. The existence of the hydride atom close to the boron atom in **3** was also indicated in the Fourier map. The spatial relationship among iridium, boron, and

hydrogen atoms in **3**, where the hydride ligand leans toward the boron center, was reproduced in an optimized structure of **3** (See Supporting Information). Similar distorted trigonal bipyramidal structures were observed for 5-coordinate 16-electron (boryl)(hydrido)chlororhodium complexes ($(\text{Pr}_3\text{P})_2\text{Rh}(\text{H})(\text{Cl})\text{Bpin}$ or Bcat (**6a,b**) in an X-ray, neutron diffraction, and computational study.^{2d,j,l} We conclude that there is little or no contribution of a B–H interaction via a σ -borane form (Figure 2) because no B–H coupling was observed in its ^1H and ^{11}B NMR spectra.¹³

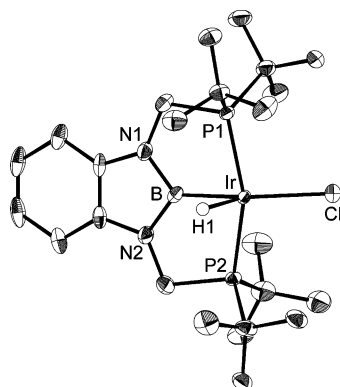


Figure 1. Crystal structure of [PBP](hydride)chloroiridium(III) complex **3** (50% thermal ellipsoids; hydrogen atoms except Ir–H were omitted for clarity). Selected interatomic distances (Å) and angles (deg): Ir–Cl, 2.3963(14); Ir–B, 1.971(6); Ir–H(1), 1.55(6); Ir–P(1), 2.3273(12); Ir–P(2), 2.3357(12); B–H(1), 1.89(6); B–N(1), 1.429(7); B–N(2), 1.437(7); B–Ir–Cl, 157.67(17); B–Ir–H(1), 63(2); Ir–B–H(1), 47.4(18); P(1)–Ir–P(2), 158.12(5); N(1)–B–N(2), 105.8(5).

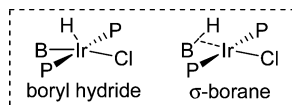
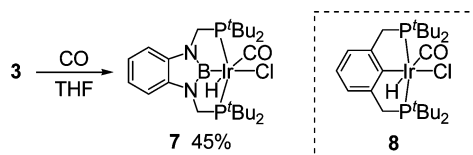


Figure 2. Two possible coordination modes in **3**.

Treatment of **3** with 1 atm of CO in THF resulted in the formation of carbonyl complex **7** (Scheme 3). A hydride signal (−8.78 ppm, t , $^2J_{\text{PH}} = 17$ Hz) and a carbonyl carbon signal (185.5 ppm, t , $^2J_{\text{PC}} = 5$ Hz) were detected in its ^1H and ^{13}C NMR spectra. The ^{11}B NMR chemical shift of 42.3 ppm also supported the formation of a boryl complex. The sharpness of the hydride signal indicates the absence of a B–H interaction. IR spectroscopy showed the characteristic CO and Ir–H peaks at 1985 and 2170 cm^{-1} , respectively.

Scheme 3. Synthesis of PBP Iridium Complex **7** and Related Compound **8**



Recrystallization of **7** from THF/hexane gave colorless crystals of **7·THF**. The ORTEP drawing is shown in Figure 3 along with selected bond lengths and angles. Both B–Ir and Ir–Cl bond lengths were slightly longer than those of **3**. Although a hydride ligand could not be located in the Fourier map, **3** may have an octahedral structure. To compare the trans-influence of the boryl ligand with that of an aryl ligand,³ PCP derivative **8** was independently synthesized from **4-H** and CO and was analyzed by X-ray crystallography.¹⁴ Crystal structures of **7** and **8** showed the same configuration, in which the chloride was located trans to boron or carbon. The longer Ir–Cl bond

length of **7** (2.5307(13) Å) than that of **8** (2.475(2) Å) revealed the stronger σ -donor ability of the PBP ligand than that of PCP.

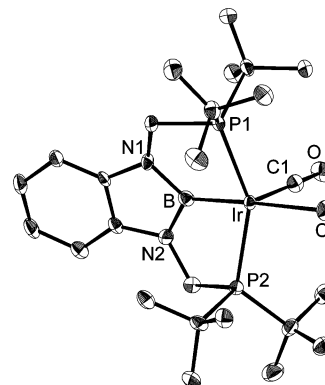
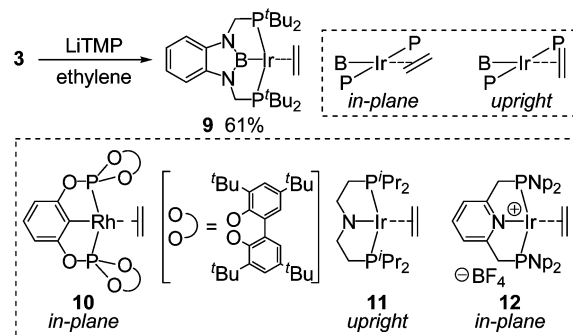


Figure 3. Crystal structure of [PBP](hydride)chloro(carbonyl)iridium(III) complex **7** (50% thermal ellipsoids; hydrogen atoms and THF of crystallization are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir–Cl, 2.5307(13); Ir–B, 2.010(6); Ir–P(1), 2.3546(13); Ir–P(2), 2.3588(13); Ir–C(1), 1.923(5); C(1)–O, 1.139(6); B–N(1), 1.423(7); B–N(2), 1.428(7); B–Ir–Cl, 174.36(16); B–Ir–C(1), 96.8(2); Cl–Ir–C(1), 88.83(15); P(1)–Ir–P(2), 150.44(4); Ir–C(1)–O, 179.3(5); N(1)–B–N(2), 106.3(4).

Ethylene complex **9** has been isolated as the first example of an ethylene-coordinated boryl complex,¹⁵ which has been proposed as an intermediate of olefin borylation. Compound **3** was converted to the ethylene-coordinated iridium(I) complex **9** in 61% yield by reaction with LiTMP under an ethylene atmosphere, as shown in Scheme 4. Coordinated ethylene signals are observed as a singlet at 3.08 and 39.1 ppm in the ^1H and ^{13}C NMR spectra, respectively. A C_{2v} symmetric structure of complex **9** was manifested by ^1H and ^{13}C NMR spectroscopy, therefore, it is unclear whether or not the ethylene ligand rotates freely in solution.

Scheme 4. Synthesis of PBP(ethylene)iridium(I) Complex **9** and Related Compounds **10–12** (TMP = 2,2,6,6-Tetramethylpiperidine, Np = Neopentyl)



In the crystal structure of **9**, shown in Figure 4, a distorted square planar structure was observed, where the P–Ir–P angle is narrow (150.67(3)°) due to the ligation of the tridentate PBP ligand. The two ethylene carbons are almost coplanar with the plane defined by PBP and the central iridium atom. In the previous example of *in-plane* ethylene coordination in diphosphite PCP pincer rhodium(I) ethylene complex **10**,¹⁶ the unusual *in-plane* conformation rather than *upright* conformation was explained by steric effects. The *in-plane* conformation of the ethylene ligand in **9** may come from its narrow P–Ir–P angle of 150.67(3)° due to the five-membered ring structure of the boryl moiety. The smaller P–Ir–P angle, compared to that of *upright* [PrPNP](ethylene)iridium complex **11**,¹⁷ would provide a sufficiently open coordination sphere for the *in-plane* conformation of ethylene

despite **9** having bulkier *t*Bu groups. Recently, *in-plane* conformation of an ethylene ligand was also observed in a [PNP]iridium complex (**12**) having less-hindered neopentyl groups on P to make a more open coordination sphere around the metal center.¹⁸

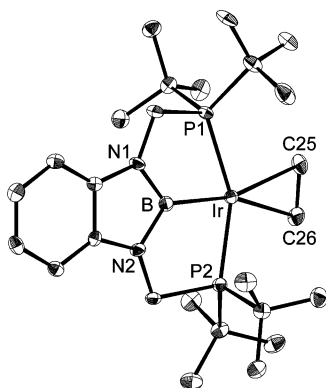


Figure 4. Crystal structure of [PBP](ethylene)iridium(I) complex **8** (50% thermal ellipsoids; hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir–B, 2.048(3); Ir–C(25), 2.205(3); Ir–C(26), 2.208(3); Ir–P(1), 2.3145(9); Ir–P(2), 2.3100(10); C(25)–C(26), 1.393(5); B–N(1), 1.443(4); B–N(2), 1.439(4); C(25)–Ir–C(26), 36.81(12); Ir–C(25)–C(26), 71.74(19); Ir–C(26)–C(25), 71.45(19); P(1)–Ir–P(2), 150.67(3); B–Ir–C(25), 161.92(14); B–Ir–C(26), 161.27(14); N(1)–B–N(2), 103.1(3).

In conclusion, we synthesized the PBP pincer ligand precursor **2** and demonstrated its complexation with iridium(I) to afford the coordinatively unsaturated [PBP](hydrido)chloroiridium complex **3** via B–H oxidative addition. The reaction of **3** with carbon monoxide produced [PBP](hydrido)chloro(carbonyl)iridium **7**. The longer Ir–Cl bond length of **7** than that of **8** revealed a stronger σ -donor ability of the PBP ligand than that of PCP. Complex **3** was also converted to [PBP](ethylene)iridium(I) complex **9** by reaction with LiTMP under an ethylene atmosphere. Applications of the easily prepared PBP pincer complexes to catalytic reactions are under investigation.

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Supporting Information Available: All experimental procedures, spectroscopic data of new compounds, details of computational study, and CIF files of **2**, **3**, and **7–9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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