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Synthesis of Pincer Iridium Complexes Bearing a Boron Atom and ^{i}Pr-Substituted Phosphorus Atoms: Application to Catalytic Transfer Dehydrogenation of Alkanes

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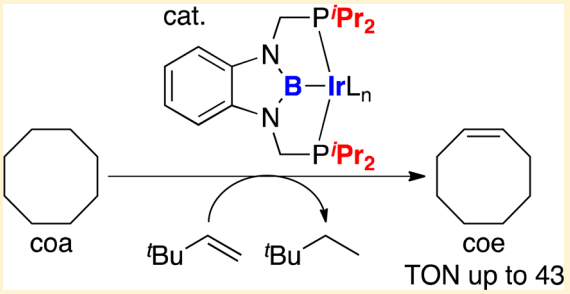
Supporting Information

ABSTRACT: An ^{i}Pr-substituted PBP-pincer ligand was synthesized and introduced to iridium metal to give ^{i}Pr-(PBP)Ir(H)Cl and ^{i}Pr-(PBP)Ir(C_2H_4) complexes. Both of these complexes were found to be moderately active for the catalytic transfer dehydrogenation of cyclooctane.

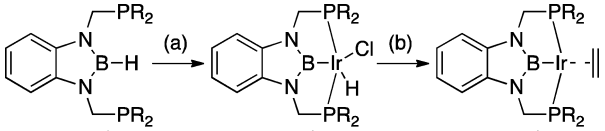


INTRODUCTION

Dehydrogenation of alkane is one of the most important reactions in industrial chemistry, because the resulting alkenes are also one of the most important resources for commodity chemicals. For the production of alkene, heterogeneous catalysts are usually used because of their advantages, such as easy separation and tolerance to high reaction temperature (500−900 °C) leading to high catalyst activity. However, the application of heterogeneous catalysts for dehydrogenation of alkanes is limited to small alkanes such as ethane,[1] propane,[2] and ethylbenzene[3] because there are selectivity issues for larger alkanes. Thus, many homogeneous catalysts[4] have been developed to apply to the dehydrogenation of higher alkanes after the discovery by Crabtree of the Ir complex $(Ph_3P)_2IrH_2(acetone)_2$, which is capable of stoichiometric dehydrogenation.[5] Among these complexes, benzene-based PCP-pincer iridium complexes[6] are recognized as being the best catalysts from the viewpoint of catalytic activity.[7] The most recent major advance for this type of catalyst from the viewpoint of catalytic activity is the development of POCSP-pincer iridium complexes, which show a TON of 5901 for transfer dehydrogenation of cyclooctane.[8] The replacement of ligand side arms in PCP-pincer systems has also been reported in the development of CCC- and PCN-pincer systems for catalytic dehydrogenation.[9] However, the catalytic activity of these dehydrogenation catalysts is still waiting to be further improved for future applications in industry.

On the other hand, we recently developed the hydroborane precursors **1a,b** (Scheme 1) of a related pincer ligand having a boron atom as one of the coordinating atoms.[10] In these reports, we demonstrated the easy introduction of these precursors to iridium to form the ^{t}Bu- or Cy-substituted (PBP)Ir(H)Cl complexes **2a,b**. Further treatment of these complexes with base in the presence of ethylene afforded the Ir(I) ethylene complexes **3a,b**. Since then, PBP-pincer ligand(s) have been introduced to Ir, Rh,[11] Ru,[12] Os,[12d] Pt,[13] Co,[14] and Ni[14b,15] to provide a wide variety of PBP-pincer complexes. Some of the PBP complexes were reported to have catalytic activity for hydrogenation of aldehyde (Ru),[12b] hydrosilylation of alkene (Pt),[13a] hydrogenation of alkene (Co, Ni),[14b] and dehydrogenation of amine−borane (Co).[14a] However, there has been no report of the transfer dehydrogenation of alkane by using PBP-pincer complexes. Since the first report of the PBP-Ir complexes, we have been making efforts to apply these complexes toward dehydrogenation of alkanes. However, complexes **2a,b** and **3a,b** were not active for catalytic dehydrogenation. Therefore, we decided to modify the alkyl

Scheme 1. Previously Reported PBP-Pincer Ligands 1a,b and Their Complexation with Iridium[a]



[a]Legend: (a) $[Ir(L)Cl]_2$ (L = 1,5-cyclooctadiene for **1a**, L = C_2H_4 for **1b**); (b) LiTMP, ethylene (TMP = 2,2,6,6-tetramethylpiperidide).

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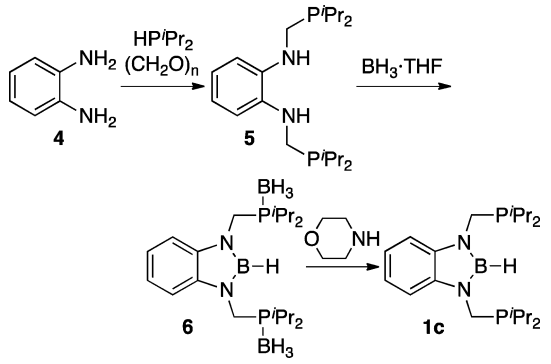
groups on the phosphorus atom to slightly smaller isopropyl groups. Herein, we report the synthesis of the isopropyl-substituted PBP-pincer ligand precursor **1c**, its complexation with iridium to form the ^{i}Pr-(PBP)Ir(H)Cl complex **2c**, its subsequent derivatization to Ir(I) ethylene complex **3c**, and the application of **3c** as a catalyst for dehydrogenation of cyclooctane.

RESULTS AND DISCUSSION

Synthesis of the ^{i}Pr-substituted PBP-pincer ligand precursor **1c** was achieved by a procedure similar to the preparation of **1a,b** (Scheme 2).[10] Reaction of *o*-phenylenediamine (**4**) with freshly

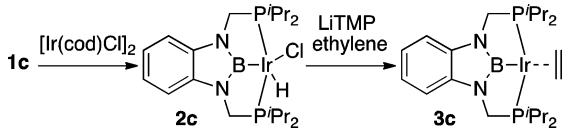
Scheme 2. Synthesis of ^{i}Pr-Substituted PBP Pincer Ligand Precursor 1c



prepared diisopropylphosphinomethanol, ^{i}Pr$_2$PCH$_2$OH, from ^{i}Pr$_2$PH and paraformaldehyde under neat conditions gave the phosphine-tethered phenylenediamine derivative **5**. Subsequent reaction of the crude mixture of **5** with BH$_3$·THF induced the formation of **6**, having a benzodiazaborole ring and borane-protected phosphorus atoms. Deprotection of the phosphine–borane moiety of **6** with morpholine afforded the hydroborane precursor **1c**.

A simple mixing of the resulting hydroborane precursor **1c** with [Ir(cod)Cl]$_2$ afforded the ^{i}Pr-substituted (PBP)Ir(H)Cl complex **2c** (Scheme 3). The subsequent treatment of **2c** with

Scheme 3. Introduction of ^{i}Pr-Substituted PBP Pincer Ligand to Ir Atom



LiTMP (lithium 2,2,6,6-tetramethylpiperidide) under an ethylene atmosphere gave the (PBP)Ir ethylene complex **3c**. Both of the products were characterized by NMR and IR spectroscopy and elemental analysis. The hydride complex **2c** showed a characteristic triplet signal at δ_H −25.34 ppm ($^{2}J_{PH}$ = 13 Hz), assignable to the hydride ligand in comparison with those of **2a,b**, in the ^{1}H NMR spectrum. The chemical shift of the hydride ligand resonated at lower field in comparison to those (ca. −40 ppm) of the previously reported (POCOP)Ir(H)Cl complexes.[16] The existence of the hydride ligand was also confirmed by an IR spectrum, possessing a characteristic vibration at 2229 cm^{-1}, supported by frequency calculations by DFT methods (see the Supporting Information). According to the magnetic inequivalency below and above the PBP-Ir plane, methylene protons between phosphorus and nitrogen atoms became inequivalent to result in the characteristic AB quartet pattern. Two phosphorus atoms in **2c** resonated as one singlet signal at δ_P 73.8 ppm in the ^{31}P NMR spectrum, as expected from the result of the previously reported **2a,b**.[10] The boron nucleus in **2c** showed a broad singlet at δ_B 33.3 ppm, being similar to those reported for **2a,b**.[10] In the ^{1}H NMR spectrum of **3c**, all four protons on the coordinating ethylene were equivalent to exhibit one singlet at δ_H 2.69 ppm. The introduction of a symmetrical ethylene molecule and loss of hydrogen chloride from **2c** led to a C_{2v}-symmetrical pattern in the ^{1}H spectrum of **3c**. Although the ^{31}P NMR chemical shift of the singlet signal of **3c** (δ_P 79.6 ppm) was similar to that of **2c**, the boron nucleus in **3c** was more deshielded, probably due to the change in the electronic structure on the iridium atom to be monovalent.

The obtained ^{i}Pr-substituted (PBP)Ir complexes **2c** and **3c** were also structurally characterized by crystallographic analysis (Figures 1 and 2, respectively). The selected bond lengths (Å)

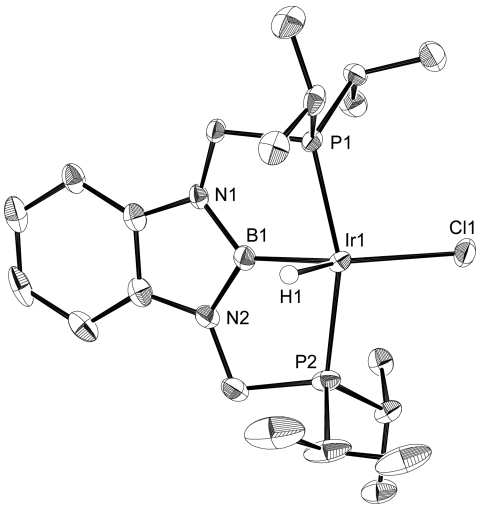


Figure 1. ORTEP drawing of **2c** (50% thermal ellipsoids; hydrogen atoms except hydride ligand omitted for clarity).

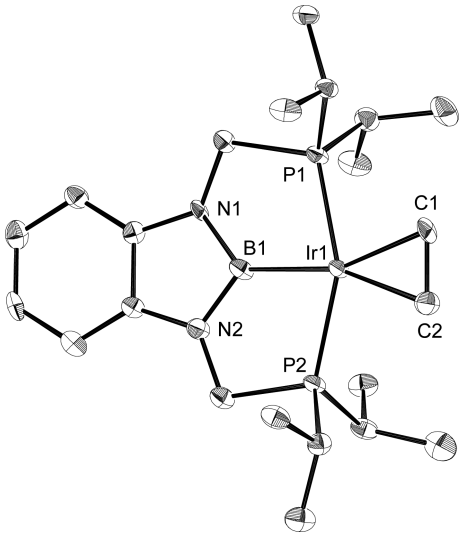


Figure 2. ORTEP drawing of **3c** (50% thermal ellipsoids; hydrogen atoms, one of the two independent molecules, and cosolvated *n*-hexane molecule omitted for clarity).

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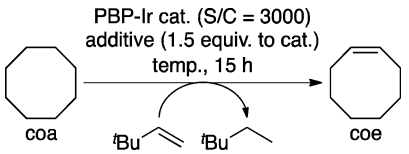
and angles (deg) of **2c** and **3c** are summarized in Table 1 with those of reference compounds **2a,b** and **3a,b**.[10] In the crystal structure of **2c**, the B−Ir bond is similar to those of **2a,b**, while the Ir−P bond in **2c** is shorter than that of **2a** and similar to that of **2b**, reflecting the steric factors of isopropyl substituents in **2c**. The Ir−Cl bond in **2c** is slightly longer than those of **2a,b**, probably being related to the B−Ir−Cl bond angles (see below). Although the B−N bonds and N−B−N angle in the benzodiazaborole ring and the P−Ir−P angle in **2c** are similar to those of **2a,b**, the B−Ir−Cl angle in **2c** is smaller than those of **2a,b**. This structural change may come from the change of steric factor among ^{t}Bu, Cy, and ^{i}Pr groups. In the crystal structure of **3c**, the Ir−B bond length is slightly longer than that of **3a** and similar to that of **3b**. In contrast, Ir−P bonds and Ir−C (ethylene ligand) bonds are shorter than those of **3a** and similar to those of **3b**, showing that the ethylene ligand can be closer to the iridium atom due to the less-hindered Cy and ^{i}Pr substituents, while the P−Ir−P angle of **3c** is between those of **3a** and **3b**. The C═C bond length of the coordinating ethylene molecule in **3c** is similar to those of **3a,b**, showing a similar strength of the back-donation from Ir(I) to the π^* orbital of ethylene. The shape of the benzodiazaborole ring in **3c** is similar to those of **3a,b**. Thus, the structural features of **2c** and **3c** showed the slightly smaller character of ^{i}Pr group in comparison to the ^{t}Bu and Cy groups.

The obtained ^{i}Pr-substituted PBP-pincer iridium complexes **2c** and **3c** were applied as catalysts for the dehydrogenation of cyclooctane (Table 2). In all entries, the doubly dehydrogenated product, cyclooctadiene, was not observed at a reaction time of 15 h. A combination of ^{i}Pr-(PBP)Ir(H)Cl complex **2c** with 1.5 equiv of ^{t}BuOLi as a base could catalyze the transfer dehydrogenation of cyclooctane (coa) at 200 °C in the presence of *tert*-butylethylene as a hydrogen acceptor, giving cyclooctene (coe) with a TON (turnover number) of 36, estimated by gas chromatography (entry 1). Changing to a stronger base with a larger alkali-metal cation led to lower TONs (entries 2 and 3). Using (trimethylsilylmethyl)lithium and LiTMP afforded even lower TONs (entries 4 and 5). Potassium hexamethyldisilazide (KHMDS) improves the TON up to 33 (entry 6). Although the tendency of the TONs with *tert*-butoxide base are similar for the reactions at 200 °C, the TONs were improved by a higher reaction temperature of 220 °C (entries 7−9). Even at 220 °C, (trimethylsilylmethyl)-lithium gave a poor TON (entry 10). In the case of LiTMP, the higher temperature showed an improvement of the TON (entry 11). Using KHMDS afforded the same TON with the case of LiTMP at 220 °C (entry 12). It should be noted that the time course of the reaction progress showed that most of the TON could be achieved around 3 h (Figure 3), indicating that most of the active catalyst decomposed at 3 h.[17] Replacement of the PBP-pincer iridium complex with **3c** enabled catalysis of the reaction even at 160 °C (entry 13). As the temperature increased, the catalyst system with **3c** gave higher TONs (entries 14−16). Thus, the present ^{i}Pr-(PBP)Ir complexes **2c** and **3c** could be applied as catalysts for the transfer dehydrogenation of cyclooctane for the first time among PBP complexes. The reason why **2c** and **3c** are active for transfer dehydrogenation of alkane, even though **2a,b** and **3a,b** are not, could be attributed to the sufficient space around

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 2c and 3c with Those of Reference Complexes 2a,b and 3a,b

	2a	2b	2c
B−Ir	1.971(6)	1.979(5)	1.976(6)
Ir−P	2.3273(12)	2.3103(13)	2.3087(13)
	2.3357(12)	2.3109(13)	2.3134(12)
Ir−Cl	2.3963(14)	2.3836(13)	2.3994(13)
Ir−H	1.55(6)	1.51(5)	1.32(5)
B−N	1.429(7)	1.428(6)	1.423(7)
	1.437(7)	1.435(6)	1.435(7)
P−Ir−P	158.12(5)	157.11(4)	158.83(5)
B−Ir−Cl	157.67(17)	144.03(16)	138.63(16)
N−B−N	105.8(5)	106.6(4)	106.7(4)
	3a	**3b**	**3c**
B−Ir	2.048(3)	2.069(5)	2.069(6)
			2.064(6)
Ir−P	2.3100(10)	2.2808(13)	2.2856(14)
			2.2884(14)
	2.3145(9)	2.2821(13)	2.2799(15)
			2.2807(15)
Ir−C	2.205(3)	2.181(5)	2.181(5)
			2.194(6)
	2.208(3)	2.199(5)	2.178(6)
			2.188(5)
C−C (C_2H_4)	1.393(5)	1.405(7)	1.402(8)
B−N	1.439(4)	1.431(7)	1.439(8)
			1.438(7)
	1.443(4)	1.434(7)	1.441(7)
			1.429(8)
P−Ir−P	150.67(3)	144.86(5)	149.45(5)
			148.66(5)
N−B−N	103.1(3)	104.8(4)	105.1(5)
			104.5(5)

Table 2. Catalytic Dehydrogenation of Cyclooctane by using PBP-pincer Ir Complexes[a]



entry	PBP-Ir cat.	additive	temp (°C)	TON[b]
1	**2c**	^{t}BuOLi	200	36[c]
2	**2c**	^{t}BuONa	200	15[c]
3	**2c**	^{t}BuOK	200	16[c]
4	**2c**	Me_3SiCH_2Li	200	5
5	**2c**	LiTMP	200	4
6	**2c**	KHMDS	200	33[c]
7	**2c**	^{t}BuOLi	220	39[c]
8	**2c**	^{t}BuONa	220	14[c]
9	**2c**	^{t}BuOK	220	14[c]
10	**2c**	Me_3SiCH_2Li	220	8
11	**2c**	LiTMP	220	43[c]
12	**2c**	KHMDS	220	42[c]
13	**3c**		160	9
14	**3c**		180	10
15	**3c**		200	23[c]
16	**3c**		220	32[c]

[a]Standard conditions: PBP-Ir cat. (3 μmol), additive (4.5 μmol), coa (10 mmol), *tert*-butylethylene (10 mmol). [b]The amount of coe was estimated by gas chromatography. [c]Estimated as an average of two experiments.

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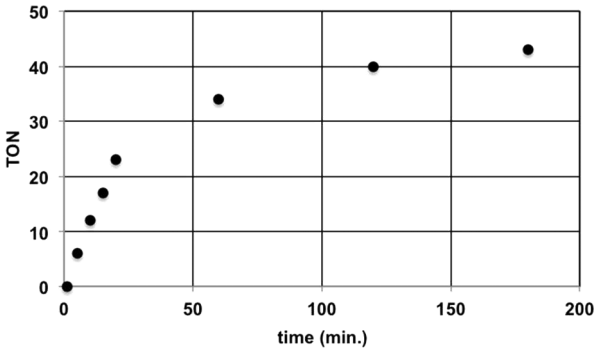
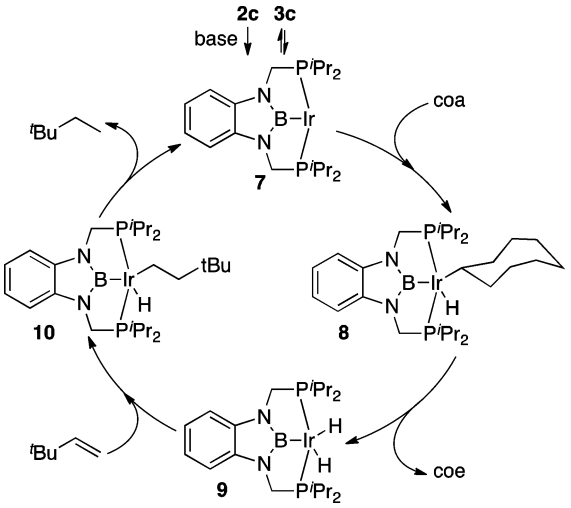


Figure 3. Time course of the TON for dehydrogenation of cyclooctane under the condition of entry 12 in Table 2. Conditions: **2c** (3 μmol), KHMDS (4.5 μmol), coa (10 mmol), *tert*-butylethylene (10 mmol). Each TON was estimated by independent experiments; the amount of coe was estimated by gas chromatography.

the Ir atom. It is also noteworthy that the present catalytic system was not active for dehydrogenation of linear *n*-octane.

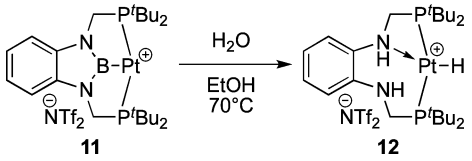
A possible mechanism for (PBP)Ir-catalyzed transfer hydrogenation of cyclooctane is illustrated in Scheme 4, according to

Scheme 4. Possible Catalytic Cycle for Transfer Dehydrogenation of Cyclooctane using ^{i}Pr-Substituted (PBP)Ir Complexes 2c and 3c



the previously studied PCP-pincer Ir systems.[7] Treatment of **2c** with base would afford the active species **7** possessing a T shape and 14 electrons as expected. Simple dissociation of ethylene ligand from **3c** would also give the same active species **7**. Oxidative addition of C−H bond of cycloocatane to **7** would form the (cyclooctyl)iridium hydride complex **8**. The subsequent *β*-hydride elimination may lead to the formation of iridium dihydride **9** with liberation of cyclooctene product. *tert*-Butylethylene would insert into the Ir−H bond of **9** to give the alkyliridium hydride complex **10**. The following C−H bond-forming reductive elimination from **10** would give *tert*-butylethane with regeneration of the 14-electron active species **7**. Considering our previous report of the loss of a boron atom from a PBP-Pt complex having the weakly coordinating ligand NTf_2 in the presence of water and ethanol (Scheme 5),[13b] the effect of the added base to **2c** may be attributed to the decomposition rate of the catalytically active species.

Scheme 5. Previously Reported Decomposition of PBP Pincer Ligand through the Loss of Boron Atom[13b]



As noted above, the previously reported ^{t}Bu- or Cy-substituted (PBP)Ir complexes **2a,b** and **3a,b** are not catalytically active for transfer dehydrogenation, while the present ^{i}Pr-(PBP)Ir complexes **2c** and **3c** are active. One of the possible reasons for this difference could be attributed to the difference in the available space around the iridium atom of the (PBP)Ir fragment in **2a−c** and **3a−c**. The monovalent (PBP)Ir fragment was extracted from the crystal structures of **3a−c**, and side views of the three fragments obtained are illustrated in Figure 4. It is difficult to see the central iridium atom in the ^{t}Bu-

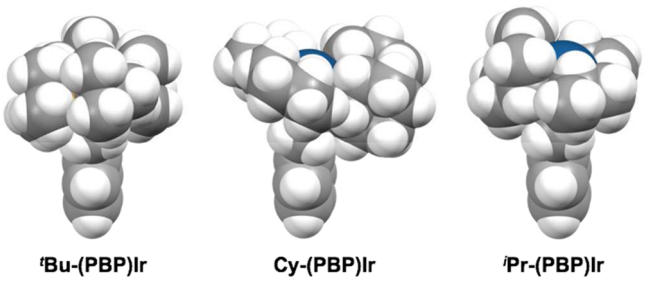


Figure 4. Side view of the R-(PBP)Ir fragment (R = ^{t}Bu, Cy, ^{i}Pr) extracted from crystal structures of **3a−c**: (blue) iridium; (gray) carbon; (white) hydrogen.

(PBP)Ir fragment of **3a** due to the existence of the ^{t}Bu groups. In the case of the Cy-(PBP)Ir fragment in **3b** and the ^{i}Pr-(PBP)Ir fragment in **3c**, the top of the central iridium atom could be seen; however, the Cy-(PBP)Ir fragment in **3b** has additional remote sterics due to the 3,4,5-positions of the cyclohexyl group. This structural difference may contribute one of the steps in the catalytic cycle to realize the catalytic activity of **2c** and **3c** in comparison with **2a,b** and **3a,b**. Even there was no direct information about the reaction mechanism and rate-determining step, a further mechanistic study with DFT calculations and improvement of the ligand structure will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. All of the preparations and manipulations involving air- and moisture-sensitive compounds were carried out under an argon atmosphere using standard Schlenk and glovebox (Miwa MFG, KIYON) techniques. All glassware were dried for 20 min in the 250 °C oven before use. Ether, CH_2Cl_2, THF, and *n*-hexane were purified by passing through a solvent purification system (Grass Contour). C_6D_6 was dried by distillation over sodium benzophenone followed by vacuum transfer. NMR spectra were recorded on JEOL ECA (500 MHz for ^{1}H, 160.5 MHz for ^{11}B, 126 MHz for ^{13}C) and Varian Mercury (400 MHz for ^{1}H) spectrometers. Chemical shifts are reported in *δ* (ppm) relative to the residual protiated solvent for ^{1}H, deuterated solvent for ^{13}C, and external BF_3·OEt_2 for ^{11}B used as references. Assignment of all signals in the ^{1}H and ^{13}C NMR spectra were based on DEPT135, HMQC, and HMBC measurements. High-resolution mass spectra were obtained by using a Xevo G2-XS QTof instrument (Waters) with ASAP ionization mode. Elemental analyses

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were performed at the A Rabbit Science Co., Ltd. IR spectra were obtained on IRAffinity-1 (Shimadzu). Melting points (mp) were determined with a MPA100 OptiMelt instrument (Tokyo Instruments, Inc.) and are uncorrected. X-ray crystallographic analyses were performed on a VariMax/Saturn CCD diffractometer.

Synthesis of 6 via the Synthetic Intermediate 5. In a glovebox, $^{i}Pr_2PH$ (7.25 g, 61.4 mmol) and paraformaldehyde (2.07 g, 68.9 mmol) were charged in a 50 mL J. Young tube and the resulting suspension was stirred for 22 h at 60 °C. After the suspension was cooled to room temperature, CH_2Cl_2 (10.0 mL) was added to the mixture. A solution of *o*-phenylenediamine (**4**; 3.36 g, 31.1 mmol) in CH_2Cl_2 (8.00 mL) was added to the reaction mixture, and the resulting solution was stirred for 18.5 h at room temperature. The solvents were evaporated under reduced pressure to give an yellow oil of **5** (11.0 g, 96%). This material was used for the next step without further purification.

5: ^{1}H NMR (500 MHz, C_6D_6) δ 0.99 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.01 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.02 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.05 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.66 (dqq, $^2J_{PH}$ = 3 Hz, $^3J_{HH}$ = 7, 7 Hz, 4H, CH(CH$_3$)$_2$), 3.09 (d, $^2J_{PH}$ = 5 Hz, 4H, N−CH_2-P), 3.43 (s, 2H, NH), 6.82 (dd, $^3J_{HH}$ = 6 Hz, 4 Hz, 2H, aromatic CH), 7.03 (dd, $^3J_{HH}$ = 6 Hz, 4 Hz, 2H, aromatic CH); ^{31}P NMR (202 MHz, C_6D_6) δ 4.4 (s).

A solution of BH_3·THF (0.95 mol/L in THF, 97.0 mL, 92.2 mmol) was added to a solution of **5** (11.0 g, 29.7 mmol) in CH_2Cl_2 (280 mL) at 0 °C. The resulting solution was stirred for 16 h at room temperature. The solvents were evaporated under reduced pressure to afford a crude product. Recrystallization of the crude product from THF/Et_2O (3/7) at −35 °C gave colorless crystals of **6** (4.99 g, 41%): ^{1}H NMR (400 MHz, C_6D_6) δ 0.92 (dd, $^3J_{PH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, 24H, CH_3), 1.09 (d, $^2J_{PH}$ = 14 Hz, 6H, P−BH_3, only observed in ^{1}H{^{11}B} spectrum), 1.77 (dqq, $^2J_{PH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, 4H, CH(CH$_3$)$_2$), 3.84 (d, $^2J_{PH}$ = 4 Hz, 4H, N−CH_2−P), 4.89 (s, 1H, BH, only observed in ^{1}H{^{11}B} spectrum), 7.06−7.08 (m, 4H, aromatic CH); ^{13}C NMR (400 MHz, C_6D_6) δ 17.2 (d, $^2J_{PC}$ = 15 Hz, CH_3), 21.3 (d, $^1J_{PC}$ = 30 Hz, CH(CH$_3$)$_2$), 37.6 (d, $^1J_{PC}$ = 31 Hz, N−CH_2−P), 110.1 (s, *ortho* to N), 120.0 (s, *meta* to N), 137.2 (s, 4°, *ipso* to N); ^{31}P NMR (202 MHz, C_6D_6) δ 37.1 (broad doublet) probably due to coupling with ^{11}B (I = 3/2) and ^{10}B (I = 3); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ − 43.1 (s, BH_3), 26.5 (s, BH); mp 130.7−132.0 °C dec; HRMS (ASAP+) calcd for $C_{20}H_{42}B_3N_2P_2$ [M] 405.3102, found 405.3113.

Synthesis of 1c. A suspension of **6** (752 mg, 1.85 mmol) and morpholine (2.50 mL, 28.7 mmol) was stirred for 6 h at 130 °C. The reaction mixture was evaporated under reduced pressure, and the residue was filtered through a pad of silica gel with Et_2O/hexane (1/1) eluent. The filtrate was evaporated under reduced pressure to give a crude product. Recrystallization of the crude product from hexane at −35.0 °C gave colorless crystals of **1c** (447 mg, 64%): ^{1}H{^{11}B} NMR (500 MHz, C_6D_6) δ 0.99 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.00 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.01 (d, $^3J_{HH}$ = 7 Hz, 12H, probably two signals were overlapped, CH_3), 1.59 (dqq, $^2J_{PH}$ = 2 Hz, $^3J_{HH}$ = 7, 7 Hz, 4H, CH(CH$_3$)$_2$), 3.83 (d, $^2J_{PH}$ = 3 Hz, 4H, N−CH_2−P), 5.11 (br s, 1H, B−H), 7.16 (dd, $^3J_{HH}$ = 6 Hz, 3 Hz, 2H, aromatic CH), 7.40 (dd, $^3J_{HH}$ = 6 Hz, 3 Hz, 2H, aromatic CH); ^{13}C NMR (400 MHz, C_6D_6) δ 19.4 (d, $^2J_{PC}$ = 12 Hz, CH$_3$), 19.8 (d, $^2J_{PC}$ = 14 Hz, CH_3), 23.3 (d, $^1J_{PC}$ = 16 Hz, CH(CH$_3$)$_2$), 40.5 (d, $^1J_{PC}$ = 19 Hz, N−CH_2−P), 110.5 (d, $^4J_{PC}$ = 6 Hz, *ortho* to N), 119.4 (s, *meta* to N), 138.4 (d, $^3J_{PC}$ < 1 Hz, 4°, *ipso* to N); ^{31}P NMR (202 MHz, C_6D_6) δ −3.8 (s); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 26.5 (s); mp 45.8−47.2 °C dec. Anal. Calcd for $C_{20}H_{37}BN_2P_2$: C, 63.50; H, 9.86; N, 7.41. Found: C, 63.65; H, 9.77; N, 7.42.

Synthesis of 2c. In a glovebox, a solution of **1c** (51.4 mg, 0.136 mmol) in THF (2 mL) was added to [Ir(cod)Cl]$_2$ (155 mg, 0.409 mmol) placed in a 4 mL vial, and the resulting solution was stirred for 20 min at room temperature to afford an orange suspension. Volatiles were removed from the suspension, and the resulting residue was dissolved in a minimum amount of THF. The THF extract was filtered, and the remaining residue was rinsed with hexane (1 mL). The resulting filtrate was evaporated to afford the crude product. Recrystallization from THF/hexane at −35.0 °C gave colorless crystals of **2c** (170 mg, 68%): ^{1}H NMR (400 MHz, C_6D_6) δ −24.87 (t, $^2J_{PH}$ = 13 Hz, 1H, Ir−H), 0.97 (d of vt, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 0.99 (d of vt, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.11 (d of vt, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.38 (d of vt, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.93 (qq of vt, $^3J_{HH}$ = 7 Hz, 7 Hz, $^2J_{PH}$ = 3 Hz, 2H, CH(CH$_3$)$_2$), 2.85 (qq of vt, $^3J_{HH}$ = 7 Hz, 7 Hz, $^2J_{PH}$ = 3 Hz, 2H, CH(CH$_3$)$_2$), 3.25 (d of vt, $^2J_{HH}$ = 12 Hz, $^2J_{PH}$ = 2 Hz, 2H, N−CHH-P), 3.39 (d of vt, $^2J_{HH}$ = 12 Hz, $^2J_{PH}$ = 3 Hz, 2H, N−CHH−P), 6.89 (dd, J = 5 Hz, 3 Hz, 2H, aromatic CH), 7.12 (dd, J = 5 Hz, 3 Hz, 2H, aromatic CH); ^{31}P NMR (202 MHz, C_6D_6) δ 73.8 (s); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 33.3 (s); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 17.3 (s, CH_3), 18.2 (s, CH_3), 18.5 (vt, $^2J_{PC}$ = 2 Hz, CH_3), 19.7 (vt, the coupling constant was too small to be estimated, CH_3), 23.8 (vt, $^1J_{PC}$ = 13 Hz, CH(CH$_3$)$_2$), 25.3 (vt, $^1J_{PC}$ = 13 Hz, CH(CH$_3$)$_2$), 39.3 (vt, $^1J_{PC}$ = 21 Hz, N-CH_2−P), 108.5 (s, *ortho* to N), 118.4 (s, *meta* to N), 140.1 (4°, vt, $^3J_{PC}$ = 7 Hz, *ipso* to N); mp 169.2−172.7 °C dec; IR (KBr) 2229 cm^{-1}. Anal. Calcd for $C_{20}H_{37}BClIrN_2P_2$: C, 39.64; H, 6.15; N, 4.62. Found: C, 39.69; H, 6.02; N, 4.50.

Synthesis of 3c. In a glovebox, a solution of lithium 2,2,6,6-tetramethylpiperidide (35.8 mg, 0.243 mmol) in benzene (1.20 mL) was added to a solution of **2c** (140 mg, 0.231 mmol) in benzene (0.900 mL) placed in a 10 mL J. Young tube. After the tube was brought out from the glovebox, the resulting solution was degassed by three cycles of freeze−pump−thaw and the tube was back-filled with ethylene. The reaction mixture was stirred for 18 h at 75 °C, and volatiles were removed under reduced pressure. The resulting residue was extracted with hexane, and the suspension was filtered through a pad of Celite. The filtrate was evaporated under reduced pressure to give a solid of **3c** (107 mg, 0.179 mmol, 78%): ^{1}H NMR (400 MHz, C_6D_6) δ 0.87 (d of vt, $^3J_{PH}$ = 13 Hz, $^2J_{HH}$ = 7 Hz, 12H, CH_3), 0.95 (d of vt, $^3J_{PH}$ = 13 Hz, $^2J_{HH}$ = 7 Hz, 12H, CH_3), 2.17 (qq of vt, $^3J_{HH}$ = 7 Hz, 7 Hz, $^2J_{PH}$ = 3 Hz, 4H, CH(CH$_3$)$_2$), 2.69 (t, $^3J_{PH}$ = 2 Hz, 4H, C_2H_4), 3.55 (vt, $^2J_{PH}$ = 2 Hz, 4H, N−CH_2−P), 7.01 (dd, $^3J_{HH}$ = 5 Hz, 3 Hz, 2H, aromatic CH), 7.18 (dd, $^3J_{HH}$ = 5 Hz, 3 Hz, 2H, aromatic CH); ^{31}P NMR (202 MHz, C_6D_6) δ 79.6 (s); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 54.6 (s); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 18.9 (vt, $^2J_{PC}$ = 2 Hz, CH$_3$), 19.0 (s, 27.0, CH$_3$) (vt, $^3J_{PC}$ = 3 Hz, CH(CH$_3$)$_2$), 37.8 (s, C_2H_4), 42.2 (vt, $^1J_{PC}$ = 21 Hz, N−CH_2−P), 108.2 (s, *ortho* to N), 117.8 (s, *meta* to N), 140.9 (vt, $^3J_{PC}$ = 8 Hz, 4°, *ipso* to N); mp 109.9−126.7 °C dec; IR (KBr) 1287 cm^{-1}. Anal. Calcd for $C_{22}H_{40}BIrN_2P_2$: C, 44.22; H, 6.75; N, 4.69. Found: C, 44.26; H, 6.61; N, 4.61.

General Procedure for Catalytic Dehydrogenation of Cyclooctane by using Complex 2c with Base. In a glovebox, a 10 mL J. Young tube was charged with base (ca. 4.5 μmol, 0.4 mg for ^{t}BuOLi, 0.4 mg for ^{t}BuONa, 0.5 mg for ^{t}BuOK, 0.7 mg for LiTMP, 0.4 mg for Me_3SiCH_2Li, 0.9 mg for KHMDS) and cyclooctane (1.202 mL, 9 mmol). In a small vial, **2c** (18.2 mg, 30.0 μmol) was dissolved in *tert*-butylethylene (11.65 mL, 90.0 mmol). An aliquot (1.165 mL, containing 3.00 μmol of **2c** and 9.00 mmol of *tert*-butylethylene) of the resulting solution was placed in the J. Young tube, and then the tube was brought out from the glovebox. The reaction mixture was stirred for 15 h at 200 or 220 °C with an aluminum-block heating stirrer. After the mixture was cooled to room temperature, dodecane (227.1 μL, 1.000 mmol) as an internal standard for GC was added to the reaction mixture. The resulting solution was analyzed by GC to estimate the yield on the basis of the independently calculated GC factor by using authentic samples.

General Procedure for Catalytic Dehydrogenation of Cyclooctane by using Complex 3c. In a glovebox, a 10 mL J. Young tube was charged with cyclooctane (1.202 mL, 9 mmol). In a small vial, **3c** (10.8 mg, 18.1 μmol) was dissolved in *tert*-butylethylene (6.99 mL, 54.0 mmol). An aliquot (1.165 mL, containing 3.02 μmol of **3c** and 9.00 mmol of *tert*-butylethylene) of the resulting solution was placed in the J. Young tube, and then the tube was brought out from the glovebox. The reaction mixture was stirred for 15 h at the indicated temperature with an aluminum-block heating stirrer. After the mixture was cooled to room temperature, dodecane (227.1 μL, 1.000 mmol) as an internal standard for GC was added to the reaction mixture. The resulting solution was analyzed by GC to estimate the yield on the

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basis of the independently calculated GC factor by using authentic samples.

Analysis of the Decomposed Product from Active Catalyst. In a glovebox, a 10 mL J. Young tube was charged with **2c** (30.6 mg, 50.5 μmol) and KHMDS (10.5 mg, 52.6 μmol). In the J. Young tube were placed cyclooctane (1.349 mL, 10.1 mmol) and *tert*-butylethylene (1.308 mL, 10.1 mmol), and then the tube was brought out from the glovebox. The reaction mixture was stirred for 6 h at 220 °C with an aluminum-block heating stirrer. After the mixture was cooled to room temperature, all of the volatiles were removed under reduced pressure. After the J. Young tube was brought back to the glovebox, the resulting residue was triturated with hexane. The hexane-soluble content of the resulting suspension was collected by filtration, and the solvent was evaporated from the filtrate to give a crude product. The crude product was dissolved in C_6D_6 to obtain NMR spectra. The ^{1}H NMR spectrum of the crude product (Figure S14 in the Supporting Information) showed several signals around 6 ppm, indicating the existence of π-allylic type protons.

Details of the X-ray Crystallographic Study. Details of the crystal data and a summary of the intensity data collection parameters for **1c**, **2c**, **3c**, and **6** are given in Table S1 in the Supporting Information. A suitable crystal was mounted with mineral oil on the glass fiber and transferred to the goniometer of a Rigaku VariMax Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). In the following procedure for analysis, Yadokari-XG 2009 was used as a graphical interface.[18] The structure was solved by direct methods (SIR-2014)[19] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014).[20] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions except for the hydrogen atom of the hydride ligand in **2c** and the BH_3 moiety in **6**, which were found in differential Fourier maps as residual peaks and were refined isotropically.

Details for Computation. All calculations were performed with the Gaussian 09 (rev. D.01) software package.[21] The molecular geometries of **2c** and **3c** were both optimized without constraints at the B3LYP level with LanL2DZ/6-31G(d) basis sets. Figure S13 in the Supporting Information shows the characteristic Ir−H vibration in **2c** and C_2H_4 vibration in **3c**. The optimized geometries are available in the Supporting Information in XYZ format.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00376.

NMR spectra of new compounds and crystal structures of synthetic intermediates (PDF)

Crystallographic data for **1c**, **2c**, **3c**, and **6** (CIF)

Cartesian coordinates of the calculated structure (XYZ)

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Notes

The authors declare no competing financial interest.

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