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Development of Highly Active Ir–PNP Catalysts for Hydrogenation of Carbon Dioxide with Organic Bases

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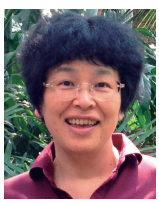
Received: September 11, 2015; Accepted: October 2, 2015; Web Released: January 15, 2016



Kyoko Nozaki

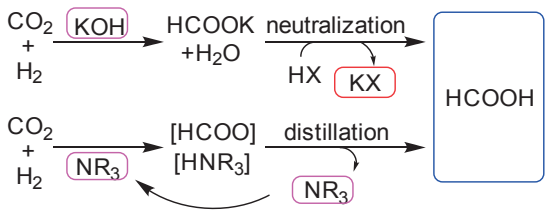
Kyoko Nozaki, born in Osaka received her B.Sc. in 1986 and her Ph.D. in 1991 from Kyoto University under the guidance of Professor Kiitiro Utimoto. During her Ph.D. study, she joined Professor Clayton H. Heathcock's group at the University of California at Berkeley as an exchange student. In 1991, she started her research career as an instructor at Kyoto University, became an associate professor in 1999, and then moved to the University of Tokyo as an associate professor in 2002. Since 2003, she is a full professor at the University of Tokyo. Her research interest is focused on development of homogeneous catalysts for polymer synthesis and organic synthesis.

Abstract

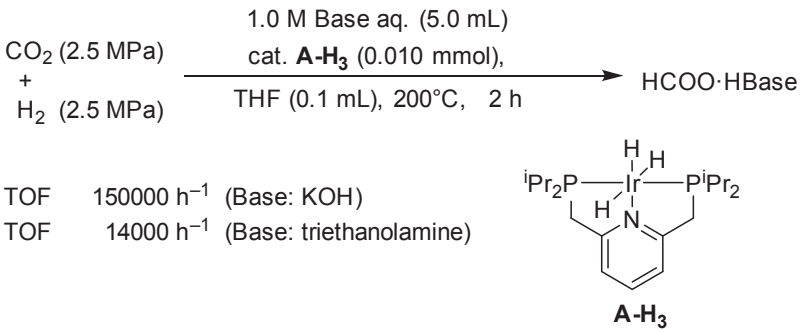
Methoxy-substituted PNP–iridium(III) complexes and pyrazine-based PNP–iridium(III) complexes were developed and used to hydrogenate carbon dioxide in the presence of triethanolamine as a base. The methoxy-substituted PNP–hydridodichloridoiridium complex (**C-HCl$_2$**) showed the highest turnover number, 160000; this is the highest value ever reported with an organic base in an aqueous medium. The reactivities of these complexes, derived from their ligand modification, were further studied. The results were as follows. (i) The pyrazine-based PNP–trihydridoiridium complex undergoes release of dihydrogen to afford dihydridoamido complex, possibly because of easy dearomatization of the pyrazine ring. This process was reversible, i.e., **B-H$_2$amido** can readily be converted back to **B-H$_3$** on exposure to dihydrogen. (ii) The *p*-methoxy-substituted dihydridochlorido complex showed facile disproportionation of the chloride anion on the iridium center; this is attributed to the electron-donating nature of the methoxypyridine backbone.

Carbon dioxide is a cheap, abundant, nontoxic, but less reactive carbon resource, compared with carbon monoxide, one of the most widely used C1 carbon sources. Catalytic hydrogenation to produce formic acid is a promising approach to CO_2 use, and has been intensively studied as an alternative to the reaction of carbon monoxide with water, which is generally used in current industrial processes.[1] The reaction of carbon dioxide with dihydrogen to produce formic acid is endoergonic by 33 kJ mol^{-1} in the gas phase (eq 1) and only slightly exoergonic, by 4 kJ mol^{-1}, in aqueous solution (eq 2).[2–6] Bases such as KOH, $NaHCO_3$, and NR_3 are therefore used to make the reaction thermodynamically more favourable (eq 3)[2–6] and to accelerate it kinetically.[7–11] Recently, homogeneous hydrogenation of carbon dioxide with various transition-metal catalysts (Ir,[2–6,8,12–24] Rh,[2–6,14,15,25] Ru,[2–6,8–11,14–16,26–38] Co,[39–43] Fe,[2–6,38,41,44–46] and others[2–6,46]) has been extensively studied. Among the catalysts developed for CO_2 hydrogenation, the trihydridoiridium–PNP pincer complex **A-H$_3$** showed the highest turnover number (TON) for formic acid production using KOH as the base (Scheme 2).[12]

The use of strong bases, however, requires an additional process, neutralization of the resulting formate salt with strong acid, to isolate formic acid; this is accompanied by formation of undesired inorganic salts (Scheme 1, top).[11] Formic acid can be isolated by simple distillation from ammonium formate, therefore the development of a highly active catalyst for hydrogenation of carbon dioxide in the presence of less volatile amine bases is desirable for industrial applications (Scheme 1, bottom).[29] After several decades of intensive research on catalysts, a significant improvement was made by



Scheme 1. Production and isolation of formic acid.



Scheme 2. CO_2 hydrogenation catalyzed by **A-H$_3$**.

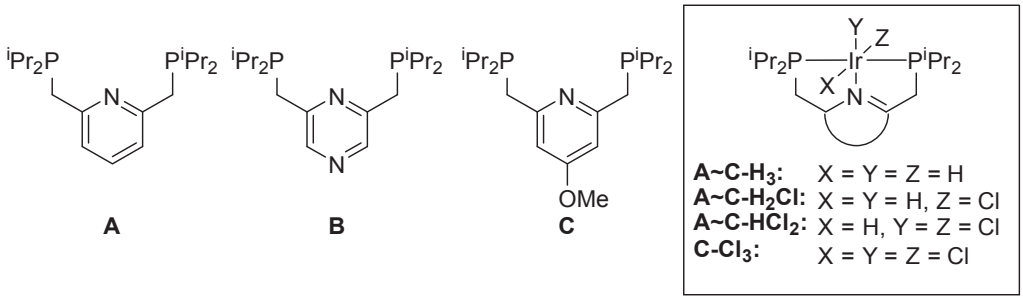


Figure 1. Ligands and iridium complexes used in this study for catalytic CO_2 hydrogenation.

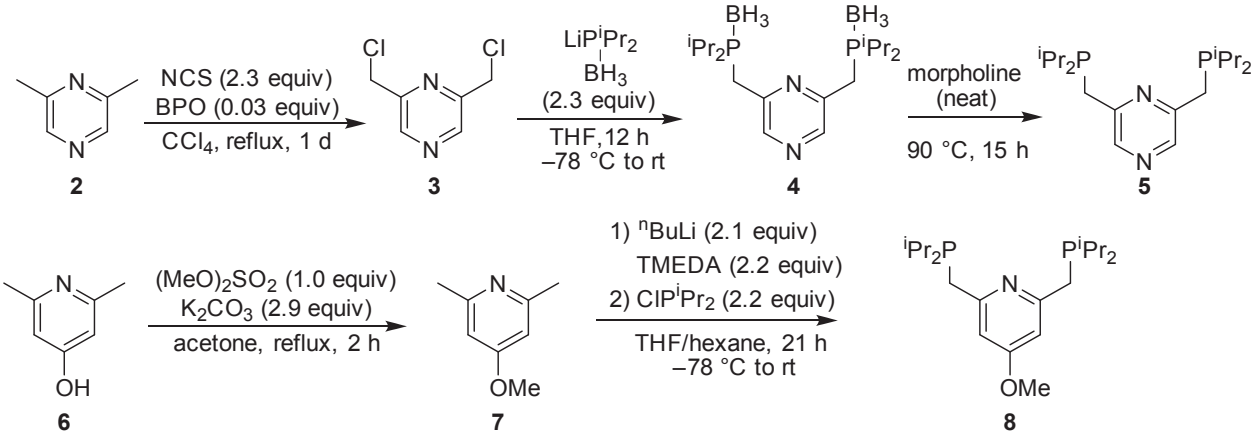
Jessop et al.; they developed [RuCl(OAc)(PMe_3)$_4$], which displayed a high initial turnover frequency (TOF, 95000 h^{-1} in 20 min) with triethylamine in supercritical carbon dioxide.[35] Recently, [Ru(PNP)(H)(Cl)CO] was reported to show a high initial TOF (1100000 h^{-1} in the initial stage, TON 200000) in the presence of DBU as a base.[30] Further improvement of the catalytic activity, however, remains a challenge, because the activities recorded with organic bases are much lower than those achieved using inorganic strong bases. For example, the high TOF (150000 h^{-1} in 2 h) we recently reported with the trihydridoiridium complex **A-H$_3$** in the presence of KOH decreased significantly when triethanolamine was used as the base (Scheme 2).[12,13]

In this study, we developed pyrazine-based PNP and methoxy-substituted PNP ligands **B** and **C**, and their iridium complexes (Figure 1). Iridium complexes containing ligands **A**–**C** and various numbers of hydride and chloride ligands were examined in hydrogenation of carbon dioxide. The methoxy-substituted PNP–hydridodichloridoiridium (**C-HCl$_2$**) showed the highest activity under the examined reaction conditions using triethanolamine as the base.

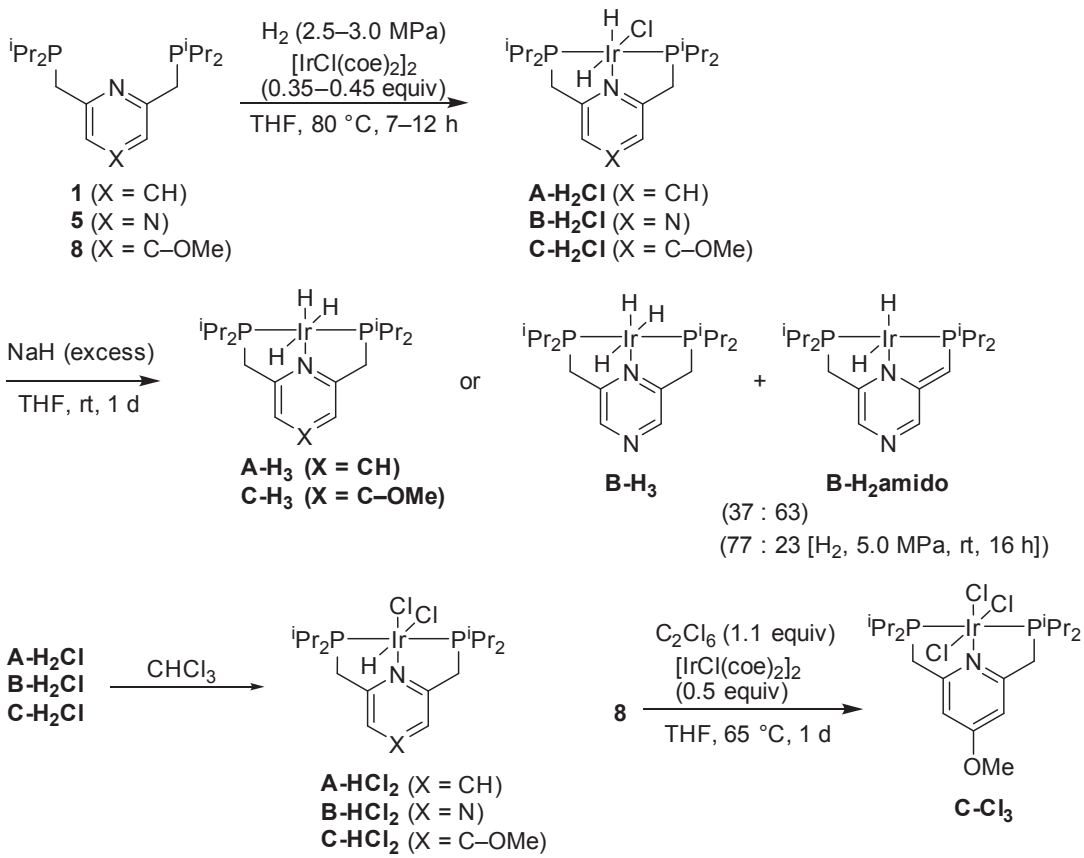
$$CO_2(g) + H_2(g) \rightarrow HCOOH(l)$$
$$\Delta G(298K) = 33\,kJ\,mol^{-1} \quad (1)$$
$$CO_2(aq) + H_2(aq) \rightarrow HCOOH(aq)$$
$$\Delta G(298K) = -4\,kJ\,mol^{-1} \quad (2)$$
$$CO_2(aq) + H_2(aq) + NH_3(aq) \rightarrow HCOO/H_4N(aq)$$
$$\Delta G(298K) = -35\,kJ\,mol^{-1} \quad (3)$$

Results and Discussion

Synthesis of Complexes. The synthetic schemes for the PNP pincer-type iridium complexes **A**–**C-H$_3$**, **A**–**C-H$_2$Cl**, **A**–**C-HCl$_2$**, and **C-Cl$_3$** are summarized in Schemes 3 and 4. The pyridine-based PNP ligand **1** (2,6-bis(diisopropylphosphinomethyl)pyridine) trihydrido complex **A-H$_3$** and dihydridochlorido complex **A-H$_2$Cl** were synthesized using a previously reported method.[12] One hydride in **A-H$_2$Cl** can be replaced by a chloride anion by reaction with excess chloroform at room temperature, to afford the hydridodichlorido complex **A-HCl$_2$**. All these complexes bearing pyridine-based ligands (complexes **A-H$_3$**–**A-HCl$_2$**) were highly stable against the loss of dihydrogen and ligand disproportionation (discussed in the following chapter) and no changes were observed after several days in tetrahydrofuran (THF) under argon at room temperature. The pyrazine-based dihydridochlorido complex **B-H$_2$Cl** was synthesized in four steps from commercially available 2,6-dimethylpyrazine (**2**; analogous to the procedure for **A-H$_2$Cl**, Schemes 3 and 4). Treatment of **B-H$_2$Cl** with chloroform resulted in formation of dichlorido complex **B-HCl$_2$**. Although nuclear magnetic resonance (NMR) spectroscopy confirmed the formation of trihydrido complex **B-H$_3$** when **B-H$_2$Cl** was treated with excess sodium hydride, **B-H$_3$** was not stable and the reaction always resulted in formation of a mixture of **B-H$_3$** and **B-H$_2$amido** dihydrido complexes after release of one dihydrogen molecule. Complex **C-H$_2$Cl**, bearing a PNP ligand with a methoxy group, was also synthesized from the methoxy-substituted ligand using a similar procedure for **A-H$_2$Cl** and **B-H$_2$Cl** shown in Schemes 3 and 4. **A-H$_2$Cl** and **B-H$_2$Cl** were stable in solution and could be isolated by single recrystallization, but the crystals of **C-H$_2$Cl** obtained by recrystallization from THF/hexane were always contaminated by a small amount of dichlorido complex **C-HCl$_2$**. The formation of **C-HCl$_2$** resulted from disproportionation of the dihydridochlorido complex (**C-H$_2$Cl**) to afford the monohydridodichlorido complex (**C-HCl$_2$**) and trihydrido complex (**C-H$_3$**) on standing in solution (vide infra). The trihydrido complex **C-H$_3$** was prepared by treatment of **C-H$_2$Cl** with sodium hydride. **C-H$_3$**, in contrast to **B-H$_3$**, is stable against dihydro-



Scheme 3. Synthesis of ligands (BPO; benzoyl peroxide. NCS; *N*-chlorosuccinimide. TMEDA; *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).

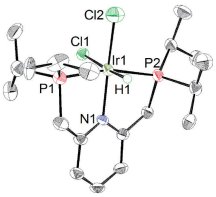
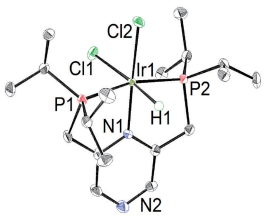
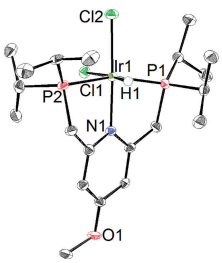


Scheme 4. Synthesis of PNP-Ir(III) complexes.

gen release, even when it is exposed to reduced pressure in THF solution. **C-H$_2$Cl** can be cleanly chlorinated by chloroform to afford the dichlorido complex **C-HCl$_2$**. The trichlorido complex **C-Cl$_3$** was also synthesized by the reaction of ligand **8** and an iridium precursor in the presence of a chlorine source, hexachloroethane. The structures of all these complexes were determined using ^{1}H, ^{31}P, and ^{13}C NMR, spectroscopies, infrared (IR) spectroscopy, and electron-spray ionization mass spectrometry (See the next section and Supplementary Information). The structures of **B-H$_2$Cl**, **A-HCl$_2$**, **B-HCl$_2$**, and **C-HCl$_2$** were elucidated by X-ray single-crystal analysis, which revealed that the chloride anion in **B-H$_2$Cl** and hydride in **A-HCl$_2$**, **B-HCl$_2$**, and **C-HCl$_2$** occupy the coordination cite *cis* to the nitrogen.

Comparison of Iridium Complexes. The use of different ligands, i.e., pyridine, pyrazine, and methoxypyridine, resulted in significant changes in the structures and spectroscopic parameters of the iridium complexes. The X-ray structures, spectroscopic parameters, and calculated natural atomic charges for complexes **A-HCl$_2$**, **B-HCl$_2$**, and **C-HCl$_2$** are shown in Table 1. Regardless of the number of chloride anions on the iridium centre, the hydride signals of the pyrazine-based complexes **B-H$_3$** (−10.08 and −18.95 ppm), **B-H$_2$Cl** (−17.77 and −21.37

Table 1. Crystal structures, observed parameters, calculated data, and catalytic activity for **A-HCl$_2$**, **B-HCl$_2$**, and **C-HCl$_2$**

	A-HCl$_2$	**B-HCl$_2$**	**C-HCl$_2$**
Crystal structure[a)]			
Hydride in ^{1}H NMR/ppm	−21.81	−20.44	−22.50
Ir–H vibration in IR/cm^{-1}	2204	2214	2197
Natural atomic charge of Ir[b)]	−0.71690	−0.71607	−0.71709
Natural atomic charge of hydride[b)]	0.12037	0.12496	0.11946
TON for hydrogenation of CO$_2$[c)]	12000	8100	38000

a) Thermal ellipsoids are drawn with 50% probability. Hydrogens on carbon atoms and solvents are omitted for clarity. Detailed information is available in the Supporting Information. b) Hybrid functional B3LYP[11] and Lanl2dz[12] on iridium, and 6-31++G(d,p) on other atoms were used as basis sets for the calculations. c) Turnover number for hydrogenation of CO$_2$ in one hour (corresponding to the data in Figure 4, blue bars).

ppm), and **B-HCl$_2$** (−20.44 ppm) were observed at significantly lower field compared with those for the corresponding pyridine-based complexes **A-H$_3$** (−10.31 and −20.22 ppm), **A-H$_2$Cl** (−18.85 and −22.18 ppm), and **A-HCl$_2$** (−21.81 ppm). In contrast, the hydride signals for the *p*-methoxy-substituted PNP complexes **C-H$_3$** (−10.47 and −20.53 ppm), **C-H$_2$Cl** (−19.05 and −22.57 ppm), and **C-HCl$_2$** (−22.50 ppm) were observed at slightly higher field than those for **A-H$_3$** (−10.31and −20.22 ppm), **A-H$_2$Cl** (−18.85 and −22.18 ppm), and **A-HCl$_2$** (−21.81 ppm). The IR absorbance of the Ir–H vibration in **A-HCl$_2$**, **B-HCl$_2$**, and **C-HCl$_2$** showed the same trend as the hydride signals, i.e., the wavenumber for **C-HCl$_2$** (2197 cm^{-1}) was lower than those for **A-HCl$_2$** (2204 cm^{-1}) and **B-HCl$_2$** (2214 cm^{-1}); this indicates that the Ir–H bonding energy in **C-HCl$_2$** was the lowest. Differences among the electronic characters were also investigated theoretically, using density functional theory (DFT) calculations.[47–52] In natural population analysis, the natural atomic charge on the iridium centre in **B-HCl$_2$** (−0.71607) was less negative than that in **A-HCl$_2$** (−0.71690). The higher electron population on the iridium and larger negative charge on the hydride in **C-HCl$_2$** (−0.71709 and 0.11946, respectively) are consistent with the electron-donating ability of methoxypyridine.

Characteristic Behaviours of Complexes B-H$_2$amido and C-H$_2$Cl in Solution. During the preparation of the complexes, we observed two characteristic behaviours, as briefly described in the previous section. Representative results are summarized in Figures 2 and 3. Complex **B-H$_2$amido** underwent facile dihydrogen addition on exposure to a dihydrogen atmosphere in C_6D_6. The ^{31}P and ^{1}H NMR spectra and the reaction are shown in Figure 2. The signals at 41 ppm in the ^{31}P NMR spectrum, and −16.7 and −22.5 ppm in the ^{1}H NMR spectrum (Figure 2(i)) indicate an unsymmetrical PNP structure and the presence of two hydrides on the iridium. The signals were assigned to **B-H$_2$amido**, by comparison with the reported data for the dihydridoamido complex **A-H$_2$amido**.[12] After standing in a dihydrogen atmosphere at room temperature for 12 h, the intensities of the ^{31}P NMR signal at 41 ppm and the hydride signals at −16.7 and −22.5 ppm decreased, accompanied by the appearance of signals corresponding to **B-H$_3$** (Figure 2(ii)), and the intensities of the signals for **B-H$_2$amido** decreased to 20% of the original level after further 11 h at 55 °C (Figure 2(iii)). This dihydrogen addition was reversible since **B-H$_3$** was cleanly converted back to **B-H$_2$amido** at 80 °C after 28 h in an argon atmosphere in THF solution (Figures 2(iii)–2(v)). Similar dihydrogen addition was also observed with **A-H$_2$amido**, but the resulting trihydrido complex **A-H$_3$** was stable against dihydrogen release even at reduced pressure.[12] This facile dihydrogen release from trihydrido complex **B-H$_3$**, which sharply contrasts with the stability of the corresponding **A-H$_3$** and **C-H$_3$** complexes, even under vacuum in solution, is attributed to the lower aromaticity of pyrazine compared to those of pyridine and methoxypyridine.[53] Although the dihydridochlorido complexes **A-H$_2$Cl** and **B-H$_2$Cl** were isolated in their pure forms by recrystallization, **C-H$_2$Cl** could only be isolated by repeated, usually three times, recrystallization, resulting in a low yield. To elucidate the different behaviour of **C-H$_2$Cl**, the precipitates and mother liquids were carefully analysed using ^{1}H and ^{31}P NMR spectroscopies (Figure 3). Recrystallization from THF/pentane solution gave crystals of **C-H$_2$Cl** contaminated with a small amount of hydridodichlorido complex **C-HCl$_2$** (Figure 3(ii)). In addition to the original dihydridochlorido complex **C-H$_2$Cl**, the hydridodichlorido complex **C-HCl$_2$** and trihydrido complex **C-H$_3$** were observed in the mother liquid (Figure 3(iii)). This facile disproportionation can be attributed to the strong electron-donating ability of the methoxypyridine ligand,[54–56] that is, the

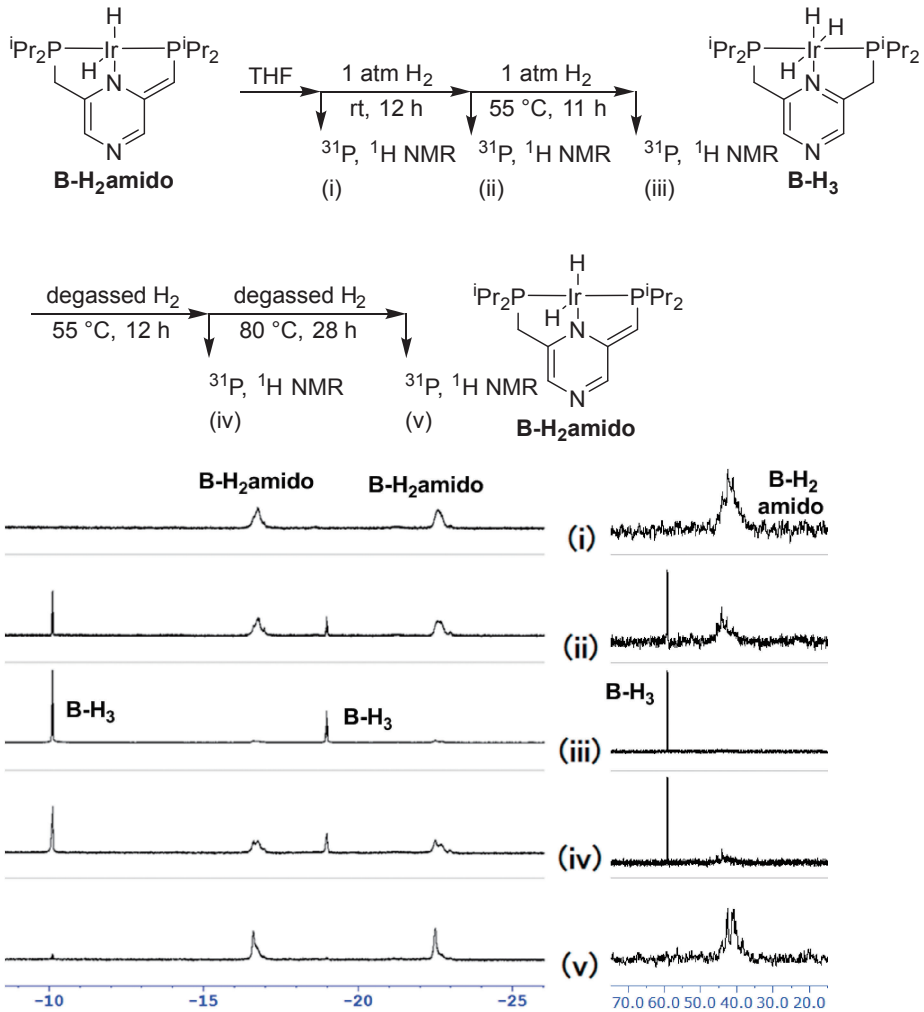


Figure 2. Interconversion of **B-H$_2$amido** and **B-H$_3$** in C_6D_6, monitored by ^{1}H NMR (hydride region, left) and ^{31}P NMR (right) spectroscopies.

methoxypyridine moiety facilitates the formation of a cationic intermediate, with release of one anionic ligand, providing an intermediate for disproportionation of anions on the iridium centre.

Hydrogenation of CO$_2$. These PNP pincer-type iridium catalysts (**A-H$_3$**–**C-Cl$_3$**) were used in the hydrogenation of carbon dioxide in aqueous triethanolamine solution; the highest TON, 160000, was achieved with **C-HCl$_2$**. Representative results are summarized in Figure 4. The homogeneity of this catalytic system was confirmed by a mercury poisoning test using **A-H$_3$** as the catalyst (see the Supporting Information). When the three trihydrido complexes **A-H$_3$**, [**B-H$_3$** + **B-H$_2$amido** (77:23)], and **C-H$_3$** were compared, **A-H$_3$** gave the highest TON after 13 h (green bars). The chloride anion lowered the catalytic activities of the pyridine-based PNP complexes (compare **A-H$_3$** with **A-H$_2$Cl** and **A-HCl$_2$**), and the TONs for **B-H$_2$Cl** and **C-H$_2$Cl** were higher than those for the corresponding trihydrido complexes [**B-H$_3$** + **B-H$_2$amido**] and **C-H$_3$**. In the case of the methoxy-substituted PNP complexes, the TON was further improved when another chloride was introduced in place of hydride (**C-HCl$_2$**, TON = 160000). A comparison of **A-HCl$_2$**, **B-HCl$_2$**, and **C-HCl$_2$** shows that the electron-donating ability of the methoxy group enhanced the catalytic activity of this catalytic hydrogenation system. This would be the result of stabilization of the cationic intermediates **C-b** and **C-d** in the proposed catalytic cycle (Scheme 5), as observed in disproportionation of the chloride anion. Although the effect of the chloride anion and amines requires further investigation, the stabilization of cationic intermediate **C-d** would lower the TS for the hydrogen splitting (**C-d** to **C-e**) in energy and eventually, the overall energy requirement ($\Delta G^{\ddagger}$) for this catalysis.[57] Further investigation of the counter anion showed that use of iodide or acetate resulted in a small drop in the TON for this catalytic system (see Supporting Information). The TON of 160000 recorded by **C-HCl$_2$** is the second highest activity ever reported in hydrogenation of carbon dioxide using amines as a base. The highest reported TON was by a PNP–Ru complex, Ru-^{t}BuPNP (TON ca. 200000),[30] with DBU as a base. However, Ru-^{t}BuPNP and the ^{i}Pr congener Ru-^{i}PrPNP showed significantly lower activities under the aqueous conditions we employed here (TON 4000 for Ru-^{t}BuPNP and 9000 for Ru-^{i}PrPNP). The introduction of one chloride into **B-H$_3$**, **C-H$_3$**, and **C-H$_2$Cl** increased the TONs, but further substitution of hydride with chloride anions resulted in considerable decreases in the activities (**B-HCl$_2$** and **C-Cl$_3$**). The TON of **C-HCl$_2$** (38000) was higher than those of **A-HCl$_2$** and **B-HCl$_2$**

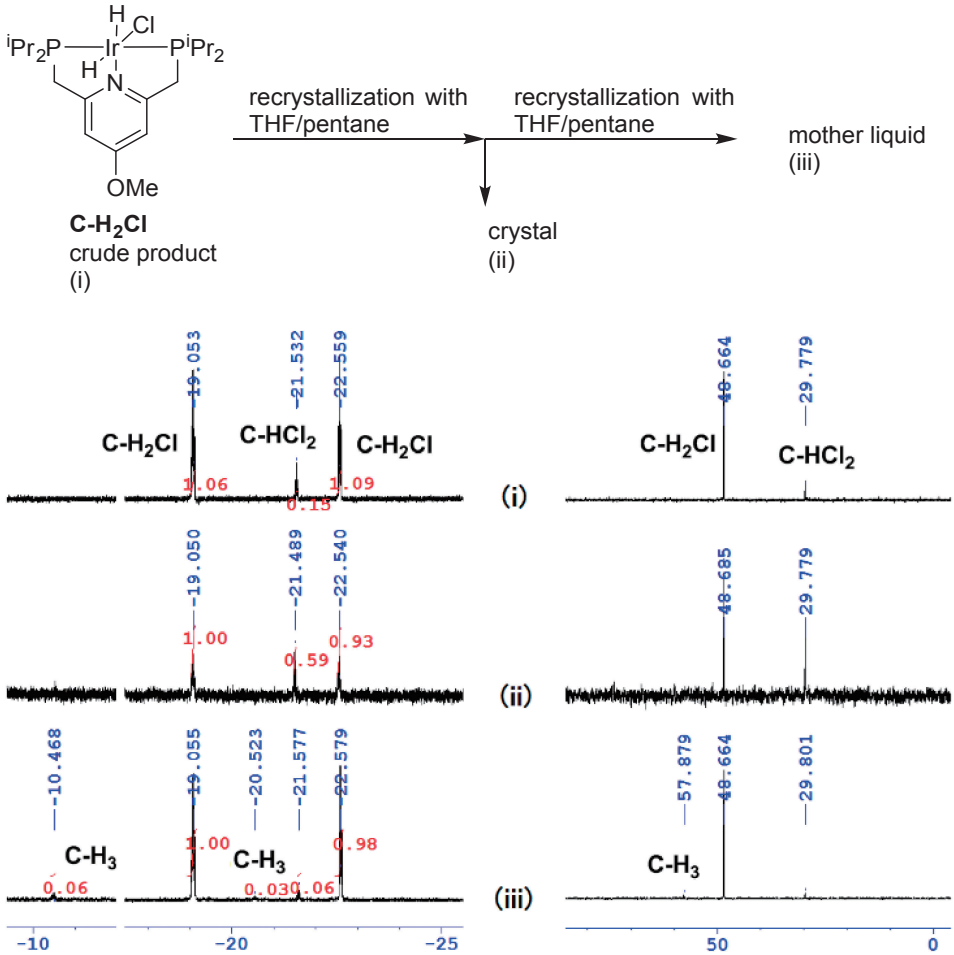


Figure 3. Structural changes in **C-H_2Cl** during recrystallization, monitored by ^{1}H NMR (hydride region, left) and ^{31}P NMR (right) spectroscopies.

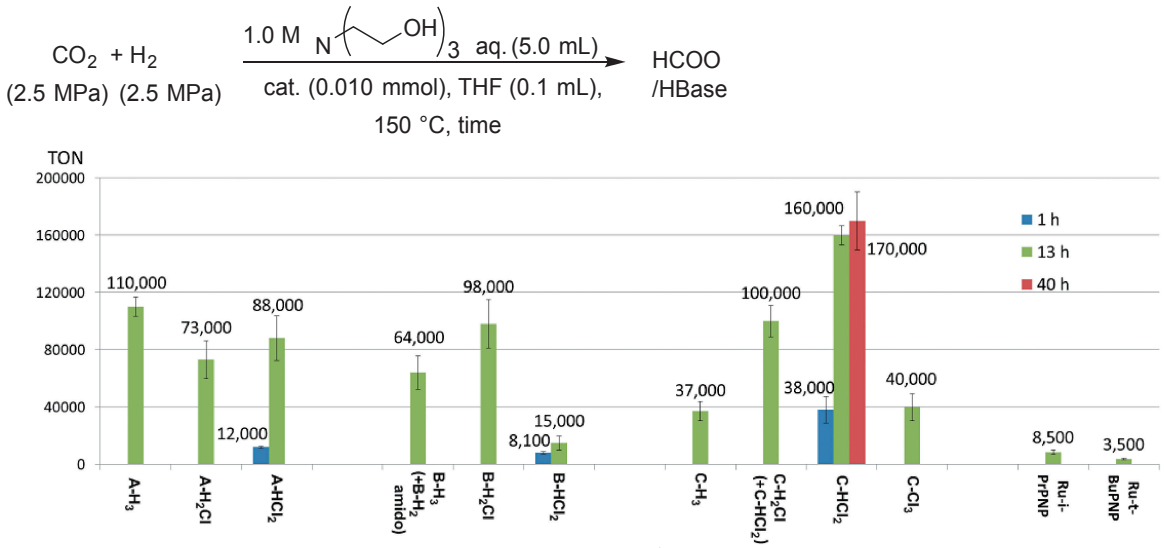
(12000 and 8100, respectively) even in the first hour, suggesting that the activity (TOF) itself, not only the robustness, was improved by the introduction of a methoxy group. The catalyst activity shows good correlation with the observed and calculated physical properties listed in the Table 1, namely, the chemical shift of hydride in ^{1}H NMR, Ir–H vibration in IR, and natural atomic charges of Ir and hydride, exhibiting the possibility to design more active catalysts. However, no significant increase was observed for a prolonged reaction time, i.e., 40 h (Figure 4, red and blue bars) while it did not reach the equilibrium (see the Supporting Information), indicating that deactivation is a potential problem for **C-HCl_2**.

Conclusion

In summary, we developed pyrazine-based PNP complexes **B** and *p*-methoxy-substituted PNP complexes **C**, which catalyse the hydrogenation of carbon dioxide in the presence of triethanolamine. These complexes showed distinct behaviours, namely facile hydrogen release (**B-H_3**) and disproportionation of anionic ligands (**C-HCl_2**). These complexes were used in catalytic CO_2 hydrogenation. The TON recorded by **A-H_3** was higher than those by **A-H_2Cl** and **A-HCl_2**. The activities of **B-H_3** and **C-H_3** were promoted by replacement of hydride ligands with chloride ligands. Among the complexes examined in this study, **C-HCl_2** gave the highest TON with an aqueous amine as a base.

Experimental

General Procedures. All manipulations involving the air- and moisture-sensitive compounds were carried out in an argon-filled glove box or using standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent or passed through solvent purification columns. Most reagents were used without further purification unless otherwise specified. NMR spectra were recorded on 500 MHz or 400 MHz spectrometers (JEOL JNM-ECP500, JEOL JNM-ECS400 and Bruker Ascend^{TM} 500). Chemical shifts are reported in ppm relative to the residual protiated solvent for ^{1}H, deuterated solvent for ^{13}C, and external 85% H_3PO_4 for ^{31}P nuclei. Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, vt = virtual triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. IR spectra were recorded on Shimadzu FTIR-8400. $[IrCl(coe)_2]_2$,[58] py-PNP (**1**),[59] (py-PNP)IrH_3 (**A-H_3**),[12] (py-PNP)IrH_2Cl (**A-H_2Cl**),[12] 2,6-bis(chloromethyl)pyrazine



a) Yield of ammonium formate was calculated based on ^{1}H NMR spectrum in D_2O with sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard. Error bar shows standard errors.

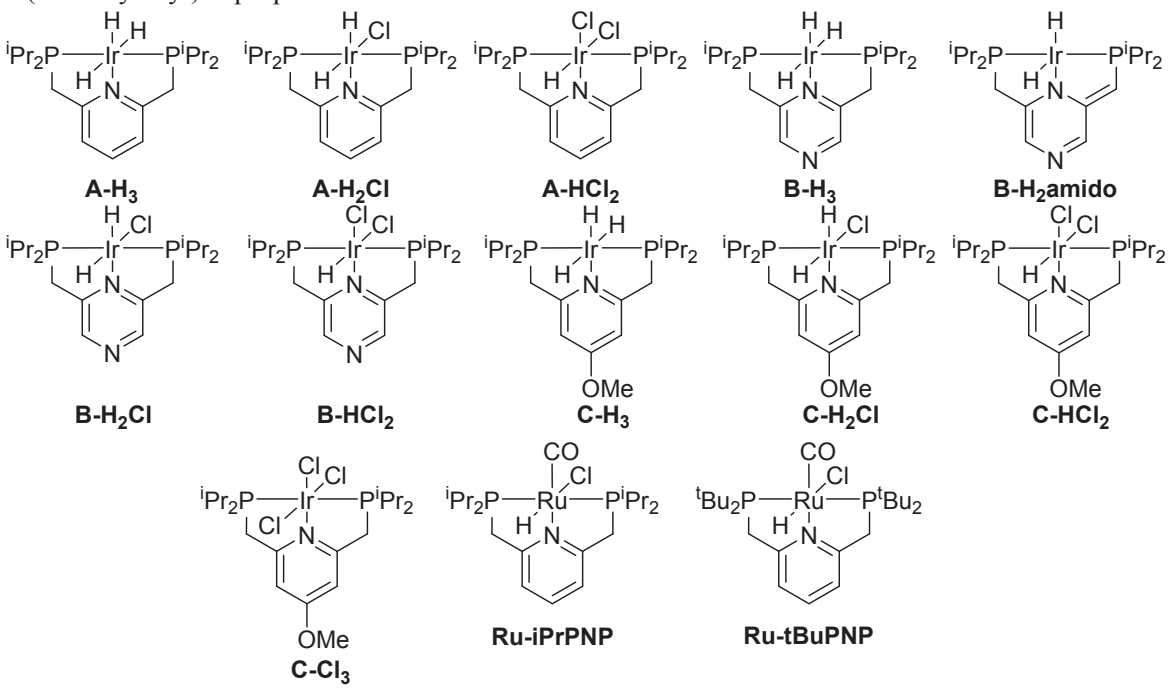
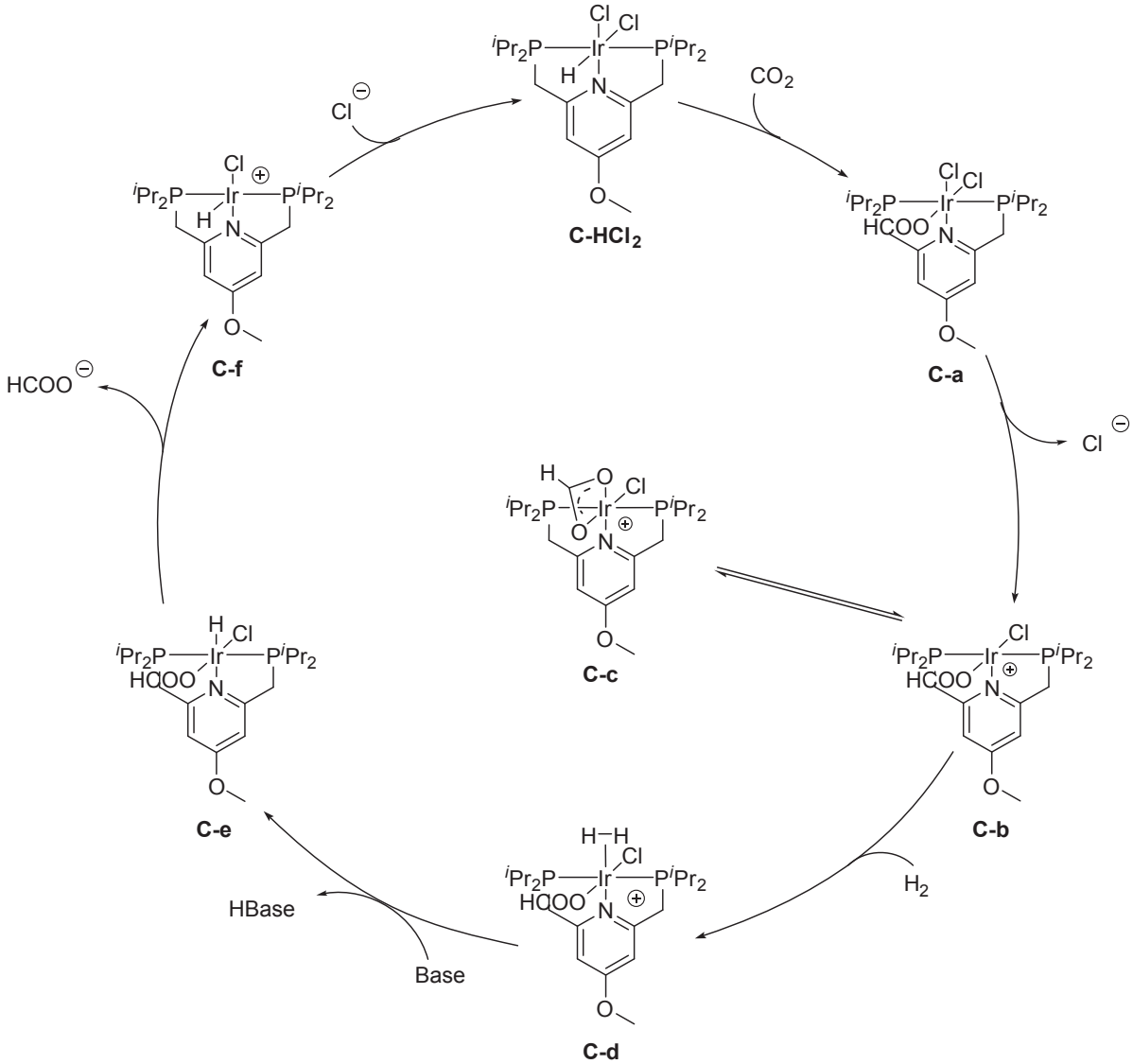


Figure 4. Hydrogenation of carbon dioxide catalyzed by Ir(III) pincer complexes using triethanolamine as base.

(**3**),[60] ^{i}Pr$_2$PH–BH$_3$,[61] (^{t}Bu)PNP–RuHCl(CO),[62] and (^{i}Pr)PNP–RuHCl(CO)[63,64] were synthesized according to the literature.

Standard Procedure for Hydrogenation of Carbon Dioxide. Catalyst (20 μmol) was dissolved in THF (4.0 mL) and diluted to 0.10 μmol mL^{-1}. To a 50 mL stainless autoclave, the solution of catalyst (100 μL, 10 nmol) and degassed aqueous triethanolamine (1.00 M, 5.00 mL) were charged and pressurized by CO_2 (2.5 MPa) and H_2 (2.5 MPa). The reaction mixture was stirred at 150 °C for 13 h. The yield of ammonium formate was calculated by ^{1}H NMR in D_2O with sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard.

Preparation of (PNP)IrH(Cl)$_2$ (A-HCl$_2$). A solution of **A-H$_2$Cl** (74 mg, 130 μmol) in $CHCl_3$ (5 mL) was stirred at 70 °C for 20 h. After the reaction time, the solvent was removed in vacuo. The residue was washed with THF (5 mL) and recrystallized from $CHCl_3$/benzene to give colourless crystal of **A-HCl$_2$** (24 mg, 42 μmol, 32%). Single crystals suitable for X-ray crystallography were obtained by recrystallization from $CHCl_3$/hexane at −35 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (t, $^3J_{HH} = 8$ Hz, 1H, pyr-H4), 7.16 (d, $^3J_{HH} = 8$ Hz, 2H, pyr-H3,H5), 3.78 (d vt, $^2J_{HH} = 17$ Hz, apparent $J = 4$ Hz, 2H, P–C*H*$_2$–pyr), 3.32 (d vt, $^2J_{HH} = 17$ Hz, apparent $J = 4$ Hz, 2H, P–C*H*$_2$–pyr), 3.16 (m, 2H, P–C*H*(CH$_3$)$_2$), 2.40 (m, 2H, P–C*H*(CH$_3$)$_2$), 1.50 (d vt, $^3J_{HH} = 8$ Hz, apparent $J = 8$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.42 (d vt, $^3J_{HH} = 7$ Hz, apparent $J = 7$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.37 (d vt, $^3J_{HH} = 8$ Hz, apparent $J = 8$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.03 (d vt, $^3J_{HH} = 7$ Hz, apparent $J = 7$ Hz, 6H, CH(C*H*$_3$)$_2$), −21.81 (t, $^2J_{PH} = 12$ Hz, 1H, Ir–*H*); ^{13}C NMR



Scheme 5. Possible catalytic cycle for CO_2 hydrogenation catalyzed by **C-HCl$_2$**.

($CDCl_3$, 126 MHz): δ 165.6 (vt, apparent $J = 4$ Hz, pyr-C2,C6), 135.9 (s, pyr-C4), 120.3 (vt, apparent $J = 5$ Hz, pyr-C3,C5), 39.9 (vt, apparent $J = 12$ Hz, P–*C*H$_2$–pyr), 25.2 (vt, apparent $J = 13$ Hz, P–*C*H(CH$_3$)$_2$), 22.8 (vt, apparent $J = 15$ Hz, P–*C*H(CH$_3$)$_2$), 19.9 (m, CH(*C*H$_3$)), 18.7 (s, CH(*C*H$_3$)), 18.3 (s, CH(*C*H$_3$)), 18.2 (s, CH(*C*H$_3$)); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 29.42; IR (powder, cm^{-1}): ν_{Ir-H} 2204. HRMS(ESI) $[M - Cl]^+$ Calcd for $C_{19}H_{36}ClIrNP_2$: 568.1641. Found: 568.1629.

Preparation of pyz-PNP–BH$_3$ (4). **pyz-PNP–BH$_3$** (**4**) was synthesized from 2,6-bis(chloromethyl)pyrazine (**3**) and ^{i}Pr$_2$-PLi–BH$_3$ according to a similar procedure in literature.[59,65]

2,6-bis(chloromethyl)pyrazine (**3**) was synthesized from 2,6-dimethylpyrazine (**2**) (3.24 g, 30 mmol) according to the literature.[61] Purification with silica-gel column chromatography (dichloromethane, hexane = 3:1, $R_f = 0.21$) gave brown oil (2.07 g, gradually decomposed under air), which contaminated 2-(dichloromethyl)-6-methylpyrazine and the crude product was used in the next step without further purification.

To a solution of ^{i}Pr$_2$PH–BH$_3$ (3.46 g, 26.2 mmol) in THF (40 mL), ^{n}BuLi (1.64 M in hexane, 16.8 mL, 27.6 mmol) was added dropwise at −78 °C and the mixture was stirred at room temperature for 13 h. A solution of the chlorinated pyrazine product **3** (2.07 g, total 11.6 mmol) in THF (18 mL) was added to the reaction mixture at −78 °C and stirred at room temperature for 12 h. After the reaction time, the reaction was quenched by adding water (0.5 mL) and the solvent was evaporated in vacuo. Water (30 mL) was added to the mixture and the product was extracted with CH_2Cl_2 (40 mL, three times). After removal of the solvent in vacuo, reprecipitation of the residue from hot methanol gave a pale yellow solid **4** (2.20 g, 5.98 mmol, 20% yield from 2,6-dimethylpyrazine).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (s, 2H, pyz-H3,H5), 3.19 (d, $^2J_{PH} = 11$ Hz, 4H, P–C*H*$_2$–pyz), 2.17–2.09 (m, 4H, P–C*H*(CH$_3$)$_2$), 1.20 (ddd, $J = 16$, 9, 6 Hz, 24H, CH(C*H*$_3$)$_2$), −0.08 to 0.73 (br m, 6H, B*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.2 ($^2J_{PC} = 6$ Hz, pyz-C2,C6), 143.7 (d, $^3J_{PC} = 2$ Hz, pyz-C3,C5), 27.8 (d, $^1J_{PC} = 25$ Hz, P–*C*H$_2$–pyz), 22.1 (d, $^1J_{PC} =$

31 Hz, P–*C*H(CH_3)$_2$), 17.2 (d, $^2J_{PC}$ = 11 Hz, CH(*C*H_3)$_2$); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 38.95–37.63 (m); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ −43.7 to −45.3 (m); Anal. Calcd for $C_{18}H_{40}B_2N_2P_2$: C, 58.73; H, 10.95; N, 7.61%. Found: C, 58.55; H, 10.98; N, 7.36%; HRMS(ESI) $[M - 2BH_3 + Na]^+$ Calcd for $C_{18}H_{34}N_2NaP_2$: 363.2095. Found: 363.2097; mp 143.0–146.5 °C (decomp.).

Preparation of pyz-PNP Ligand (5). Ligand **5** was synthesized from pyz-PNP–BH_3 (**4**) according to a similar procedure in literature.[66] A suspension of pyz-PNP–BH_3 (**4**) (478 mg, 1.30 mmol) in degassed morpholine (10 mL) was heated at 90 °C for 15 h. The reaction progress was monitored by ^{31}P and ^{11}B NMR. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The product was extracted with toluene (5 mL, 2 mL × 3). The combined organic phase was washed with degassed water (2 mL). Concentration of the organic phase gave brown oil (360 mg, 81%), which was used in the next step without further purification.

^{1}H NMR (400 MHz C_6D_6): δ 8.43 (s, 2H, pyz-H5), 2.75 (d, $^2J_{PH}$ = 1 Hz, 4H, P–C*H*$_2$–pyz), 1.62 (m, 4H, P–C*H*(CH$_3$)$_2$), 1.01–0.95 (m, 24H, CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.9 (d, $^2J_{PC}$ = 9 Hz, pyz-C2,C6), 142.2 (d, $^3J_{PC}$ = 7 Hz, pyz-C3,C5), 29.9 (d, $^1J_{PC}$ = 26 Hz, P–*C*H$_2$–pyz), 23.9 (d, $^1J_{PC}$ = 16 Hz, P–*C*H(CH$_3$)$_2$), 19.9 (d, $^2J_{PC}$ = 15 Hz, CH(*C*H$_3$)$_2$), 19.2 (d, $^2J_{PC}$ = 12 Hz, CH(*C*H$_3$)$_2$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 12.80 (s); HRMS(ESI) $[M + H]^+$ Calcd for $C_{18}H_{35}N_2P_2$: 341.2275. Found: 341.2266.

Preparation of (pyz-PNP)IrH$_2$Cl (B-H$_2$Cl). **B-H$_2$Cl** was synthesizd from pyz-PNP (**5**) according to a similar procedure in literature.[12] To a 50 mL stainless autoclave, $[IrCl(coe)_2]_2$ (342 mg, 0.38 mmol), pyz-PNP ligand (**5**, 368 mg, 1.08 mmol), and THF (15 mL) were charged under argon atmosphere. The mixture was pressurized by hydrogen (2.5 MPa) and stirred at 80 °C for seven hours. The solvent was removed in vacuo and the residue was reprecipitated from THF/hexane. After washing the residue with hexane, colourless solid was obtained. **B-H$_2$Cl** (354 mg, 750 µmol, 80%). Single crystals suitable for X-ray crystallography were obtained by recrystallization from THF/pentane at −35 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.04 (s, 2H, pyz-H3,H5), 3.18 (d vt, $^2J_{HH}$ = 17 Hz, apparent J = 4 Hz, 2H, P–C*H*$_2$–pyz), 2.88 (m, 2H, P–C*H*(CH$_3$)$_2$), 2.59 (d vt, $^2J_{HH}$ = 17 Hz, apparent J = 4 Hz, 2H, P–C*H*$_2$–pyz), 1.59 (m, 2H, P–C*H*(CH$_3$)$_2$), 1.49 (d vt, $^3J_{HH}$ = 8 Hz, apparent J = 8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d vt, $^3J_{HH}$ = 7 Hz, apparent J = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.03 (d vt, $^3J_{HH}$ = 8 Hz, apparent J = 8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.68 (d vt, $^3J_{HH}$ = 7 Hz, apparent J = 7 Hz, 6H, CH(C*H*$_3$)$_2$), −17.77 (td, $^2J_{HH}$ = 8 Hz, $^2J_{PH}$ = 13 Hz, 1H, Ir–*H*), −21.37 (td, $^2J_{HH}$ = 8 Hz, $^2J_{PH}$ = 15 Hz, 1H, Ir–*H*); ^{13}C NMR (C_6D_6, 101 MHz): δ 157.8 (vt, apparent J = 5 Hz, pyz-C2,C6), 140.5 (vt, apparent J = 5 Hz, pyz-C3,C5), 40.0 (vt, apparent J = 12 Hz, P–*C*H$_2$–pyz), 24.9 (m, P–*C*H(CH$_3$)$_2$), 21.1 (br s, CH(*C*H$_3$)), 20.6 (vt, apparent J = 3 Hz, CH(*C*H$_3$)), 19.0 (s, CH(*C*H$_3$)), 17.2 (s, CH(*C*H$_3$)); ^{31}P NMR (C_6D_6, 162 MHz): δ 48.9; IR (KBr, cm^{-1}): ν_{Ir-H} 2176, 2098. HRMS(EI) $[M + MeCN - Cl]^+$ Calcd for $C_{20}H_{39}IrN_3P_2$: 576.2248. Found: 576.224.

Preparation of (pyz-PNP*)Ir(H)$_2$ (B-H$_2$amido). **B-H$_2$amido** was synthesize from **B-H$_2$Cl** according to a similar procedure in literature.[12]

To a solution of **B-H$_2$Cl** (13 mg, 198 mmol) in THF (4 mL), finely ground CsOH–H_2O (100 mg, 596 mmol) was added and the resulting mixture was stirred at room temperature for one day. During that time, the suspension turned to dark red solution. After completion of the reaction was confirmed by ^{31}P NMR, the solvent was removed under reduced pressure. The product was extracted with toluene and recrystallized from benzene/heptane to give red solid **B-H$_2$amido** (65 mg, 121 µmol, 62%). The signals of NMR spectra were broadened and it implied an equilibrium between multiple species. The full assignment of the each signal was unsuccessful because of the broadness, and ^{31}P NMR is shown in the Supporting Information.

Preparation of Mixture of (pyz-PNP*)Ir(H)$_2$ (B-H$_2$amido) and (pyz-PNP)IrH$_3$ (B-H$_3$). This reaction is performed according to a similar procedure in literature.[12]

To a solution of **B-H$_2$Cl** (113 mg, 0.20 mol) in THF (4 mL), NaH (100 mg, 4.2 mmol) was added and the resulting mixture was stirred at room temperature for one day. During that time, the suspension turned to dark red solution. After confirmation of the reaction completion by ^{31}P NMR, the solvent was removed in vacuo. The residue was extracted with toluene and recrystallized from cold hexane to give red crystal (65 mg, 121 µmol, 62%), mixture of **B-H$_3$** and **B-H$_2$amido**. The ratio of the **B-H$_3$** and **B-H$_2$amido** was different in each experiment. The ratio of **B-H$_3$** increased by treating the reaction mixture (23 mg) in THF-d_8 (1.5 mL) with H_2 (5.0 MPa) at room temperature for 17 h. Data of **B-H$_3$** is shown below. ^{1}H NMR (THF-d_8, 500 MHz): δ 8.16 (s, 2H, pyz-H3,H5), 3.30 (vt, apparent J = 4 Hz, P–C*H*$_2$–pyz, 4H), 1.91 (m, P–C*H*(CH$_3$)$_2$, 4H), 1.14 (d vt, $^3J_{HH}$ = 8 Hz, apparent J = 8 Hz, 12H), 1.07 (d vt, $^3J_{HH}$ = 7 Hz, apparent J = 7 Hz, 12H), −10.70 (td, $^2J_{HH}$ = 5 Hz, $^2J_{PH}$ = 17 Hz, 2H), −19.83 (tt, $^2J_{HH}$ = 5 Hz, $^2J_{PH}$ = 14 Hz, 1H); ^{13}C NMR (THF-d_8, 101 MHz): δ 158.3 (vt, apparent J = 5 Hz, pyz-C2,C6), 139.5 (vt, apparent J = 5 Hz, pyz-C3,C5), 40.9 (vt, apparent J = 12 Hz, P–*C*H$_2$–pyz), 27.6 (vt, apparent J = 15 Hz, P–*C*H(CH$_3$)$_2$), 19.7 (m, CH(*C*H$_3$)$_2$), 18.8 (s, CH(*C*H$_3$)); ^{31}P{^{1}H} NMR (THF-d_8, 202 MHz): δ 57.9; IR (KBr, cm^{-1}): ν_{Ir-H} 2094, 1717. HRMS(ESI) [**B-H$_3$** + MeCN − H]$^+$ Calcd for $C_{20}H_{39}IrN_3P_2$: 576.2248. Found: 576.2273.

Preparation of (yz-PNP)IrH(Cl)$_2$ (B-HCl$_2$). A solution of **B-H$_2$Cl** (79 mg, 140 µmol) in $CHCl_3$ (5 mL) was stirred at 70 °C for one day. After the reaction, the solvent was removed in vacuo. The residue was reprecipitated from THF/pentane and recrystallized from THF/pentane to give light brown crystals of **B-HCl$_2$** (18 mg, 32 µmol, 23%). Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene/hexane at −35 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.35 (s, 2H, pyz-H3,H5), 3.67 (d vt, $^2J_{HH}$ = 17 Hz, apparent J = 4 Hz, 2H, P–CH$_2$–pyz), 3.24 (d vt, $^2J_{HH}$ = 17 Hz, apparent J = 4 Hz, 2H, P–CH$_2$–pyz), 3.19 (m, 2H, P–CH(CH$_3$)$_2$), 2.42 (m, 2H, P–CH(CH$_3$)$_2$), 1.51 (d vt, $^3J_{HH}$ = 8 Hz, apparent J = 8 Hz, 6H, CH(CH$_3$)$_2$), 1.43 (d vt, $^3J_{HH}$ = 7 Hz, apparent J = 7 Hz, 6H, CH(CH$_3$)$_2$), 1.37 (d vt, $^3J_{HH}$ = 8 Hz, apparent J = 8 Hz, 6H, CH(CH$_3$)$_2$), 1.05 (d vt, $^3J_{HH}$ = 8 Hz, apparent J = 8 Hz, 6H), −20.44 (t, $^2J_{PH}$ = 12 Hz, 1H, Ir–H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 160.5 (vt, apparent J = 4 Hz, pyz-C2,C6), 141.0 (vt, apparent J = 5 Hz, pyz-C3,C5), 36.6 (vt, apparent J = 11 Hz, P–CH$_2$–pyz), 25.4 (vt,

apparent $J = 14$ Hz, P–CH(CH_3)$_2$), 23.1 (vt, apparent $J = 15$ Hz, P–CH(CH_3)$_2$), 19.8 (s, CH(CH_3)), 18.6 (s, CH(CH_3)), 18.3 (s, CH(CH_3)), 18.1 (s, CH(CH_3)); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 30.82; IR (powder, cm^{-1}): ν_{Ir-H} 2214. HRMS(ESI) $[M - HCl_2]^+$ Calcd for $C_{18}H_{34}IN_2P_2$: 533.1826. Found: 533.1805.

Preparation of 4-Methoxy-2,6-dimethylpyridine (7). 4-Methoxy-2,6-dimethylpyridine (**7**) was synthesizd from 4-hydroxy-2,6-dimethylpyridine (**6**) (3.24 g, 30 mmol) according to a similar procedure in literature.[67]

A suspension of **6** (1.85 g, 15.0 mmol), dimethyl sulfate (1.47 mL, 15.5 mmol) and potassium carbonate (6.09 g, 44.1 mmol) in anhydrous acetone (56 mL) was heated under reflux for 2 h. After cooling to 0 °C the mixture was filtered through a short plug of silica on a glass filter. The filtrate was concentrated to provide **7** (1.53 g, 11.1 mmol, yield) as yellow spectrooscopic data were consistent with the literature.[68]

Preparation of *p*OMe-PNP Ligand 8. 4-Methoxy-PNP was synthesized from 4-methoxy-2,6-dimethylpyridine (**7**) according to a similar procedure in literature.[69,70]

To a solution of 2,6-dimethyl-4-methoxypyridine 7 (686 mg, 5.00 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.6 mL, 11 mmol) in Et_2O (13 mL), *n*BuLi (2.66 M in hexane, 4.0 mL, 10.6 mmol) was added dropwise at 0 °C and the mixture was allowed to warm to room temperature with stirring for 5 h. A solution of ^{i}Pr$_2$PCl (1.70 g, 11.2 mmol) in Et_2O (10 mL) was added to the resulting mixture dropwise at −78 °C and stirred at room temperature for 21 h. After the reaction, the resulted solid was removed by filtration through a pad of Celite, and the filtrate was concentrated by evaporation. The obtained crude product was purified by passing through a short plug of silica gel on a glass filter with Et_2O as an eluent. The solvent was removed to give light brown oil of **8** (1.64 g), which was used in the next step without further purification. ^{1}H NMR (400 MHz, C_6D_6): δ 6.78 (s, 2H, pyr-H3,H5), 3.20 (s, 3H, O–CH_3), 2.98 (d, $^2J_{PH} = 1$ Hz, 4H, P–CH_2–pyr), 1.79–1.67 (m, 4H, P–CH(CH_3)$_2$), 1.11–1.03 (m, 24H, CH(CH_3)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5 (s, C–O–CH_3), 162.0 (d, $^2J_{PC} = 10$ Hz, pyr-C2,C6), 106.8 (d, $^3J_{PC} = 7$ Hz, pyr-C3,C5), 54.3 (s, O–CH_3), 33.2 (d, $^1J_{PC} = 23$ Hz, P–CH_2–pyr), 23.9 (d, $^1J_{PC} = 16$ Hz, P–CH(CH_3)$_2$), 19.9 (d, $^2J_{PC} = 14$ Hz, CH(CH_3)$_2$), 19.3 (d, $^2J_{PC} = 11$ Hz, CH(CH_3)$_2$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 11.64; HRMS(ESI) $[M + H]^+$ Calcd for $C_{20}H_{38}NOP_2$: 370.2429. Found: 370.2417.

Preparation of (*p*OMe-PNP)IrH$_2$Cl (C-H$_2$Cl). **C-H$_2$Cl** was synthesized from *p*-OMe-PNP (**5**) according to a similar procedure in literature.[12]

To a 50 mL stainless autoclave, $[IrCl(coe)_2]_2$ (448 mg, 0.500 mmol), *p*OMe-PNP (**8**, 406 mg, 1.10 mmol), and THF (20 mL) were charged under argon atmosphere. The mixture was pressurized by hydrogen (3.0 MPa) and stirred at 80 °C for 12 h. The solvent was removed in vacuo and the residue was reprecipitated from THF/hexane. The residue was washed with hexane to give a pale-yellow solid. Because of the facile disproportionation in the reaction condition and high crystallinity of **C-HCl$_2$**, a mixture of **C-H$_2$Cl** and **C-HCl$_2$** (414 mg) was obtained (**C-H$_2$Cl**/**C-HCl$_2$** = 1/0.16). Subsequent recrystallizations from THF/pentane twice and extraction with THF gave a mixture of **C-H$_2$Cl** and **C-HCl$_2$** at the ratio of 1/0.07.

^{1}H NMR (THF-d_8, 500 MHz): δ 6.87 (s, 2H, pyr-H3,H5), 3.80 (s, 3H, OCH_3), 3.75 (d vt, $^2J_{HH} = 16$ Hz, apparent $J = 4$ Hz, 2H, P–CH_2–pyr), 3.48 (d vt, $^2J_{HH} = 17$ Hz, apparent $J = 4$ Hz, 2H, P–CH_2–pyr), 2.77 (m, 2H, P–CH(CH$_3$)$_2$), 1.98 (m, 2H, P–CH(CH$_3$)$_2$), 1.34 (d vt, $^3J_{HH} = 8$ Hz, apparent $J = 8$ Hz, 6H, CH(CH_3)$_2$), 1.30 (d vt, $^3J_{HH} = 7$ Hz, apparent $J = 7$ Hz, 6H, CH(CH_3)$_2$), 1.09 (d vt, $^3J_{HH} = 8$ Hz, apparent $J = 8$ Hz, 6H, CH(CH_3)$_2$), 0.88 (d vt, $^3J_{HH} = 7$ Hz, apparent $J = 7$ Hz, 6H, CH(CH_3)$_2$), −19.83 (td, $^2J_{HH} = 8$ Hz, $^2J_{PH} = 13$ Hz, 1H, Ir–*H*), −23.01 (td, $^2J_{HH} = 8$ Hz, $^2J_{PH} = 15$ Hz, 1H, Ir–*H*); ^{13}C NMR (C_6D_6, 126 MHz): δ 164.9 (s, pyr-C4), 164.4 (vt, apparent $J = 4$ Hz, pyr-C2,C6), 105.4 (vt, apparent $J = 5$ Hz, pyr-C3,C5), 54.9 (s, OCH_3), 43.9 (vt, apparent $J = 12$ Hz, P–CH_2–pyr), 24.8 (m, P–CH(CH$_3$)$_2$), 21.2 (vt, apparent $J = 3$ Hz, CH(CH_3)), 20.8 (vt, apparent $J = 3$ Hz, CH(CH_3)), 19.3 (s, CH(CH_3)), 17.4 (s, CH(CH_3)); ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ 48.7; IR (KBr, cm^{-1}): ν_{Ir-H} 2176, 2098. HRMS(ESI) $[M - Cl]^+$ Calcd for $C_{20}H_{39}IrNOP_2$: 564.2136. Found: 564.2134.

Preparation of (*p*OMe-PNP)Ir(H)$_3$ (C-H$_3$). **C-H$_3$** was synthesized from **C-H$_2$Cl** according to a similar procedure in literature.[12]

To a solution of **C-H$_2$Cl** (+**C-HCl$_2$**) (100 mg, 0.17 mmol) in THF (10 mL), NaH (50 mg, 2 mmol) was added and the resulting mixture was stirred at room temperature for 1 day. During that time, the suspension turned to a dark red solution. After confirmation of the completion by ^{31}P NMR, the solvent was removed in vacuo. The residue was extracted with hexane and recrystallized from cold hexane to afford off-white solid (**C-H$_3$**, 21 mg, 37 μmol, 22%).

^{1}H NMR (C_6D_6, 500 MHz): δ 6.25 (s, 2H, pyr-H3,H5), 3.12 (s, 3H, OCH_3), 3.01 (vt, apparent $J = 3$ Hz, 2H, P–CH_2–pyr), 1.85 (m, 2H, P–CH(CH_3)$_2$), 1.28 (d vt, $^3J_{HH} = 8$ Hz, apparent $J = 8$ Hz, 12H, CH(CH_3)$_2$), 1.18 (d vt, $^3J_{HH} = 7$ Hz, apparent $J = 7$ Hz, 12H, CH(CH_3)$_2$), −10.47 (td, $^2J_{PH} = 17$ Hz, $^2J_{HH} = 5$ Hz, 2H, Ir–H), −20.53 (tt, $^2J_{PH} = 14$ Hz, $^2J_{HH} = 5$ Hz, 1H, Ir–H); ^{13}C NMR (C_6D_6, 126 MHz): δ 163.9 (vt, apparent $J = 4$ Hz, pyr-C2,C6), 163.5 (s, pyr-C4), 104.6 (vt, apparent $J = 5$ Hz, pyr-C3,C5), 54.7 (s, OCH_3), 45.1 (vt, apparent $J = 12$ Hz, P–CH_2–pyr), 27.1 (vt, apparent $J = 15$ Hz, P–CH(CH_3)$_2$), 20.0 (vt, apparent $J = 3$ Hz, CH(CH_3)$_2$), 19.1 (s, CH(CH_3)$_2$); ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 57.8; IR (KBr, cm^{-1}): ν_{Ir-H} 2083, 1686. HRMS(ESI) $[M - H]^+$ Calcd for $C_{20}H_{39}IrNOP_2$: 564.2136. Found: 564.2111.

Preparation of (*p*OMe-PNP)IrH(Cl)$_2$ (C-HCl$_2$). A solution of **C-H$_2$Cl** (+**C-HCl$_2$**) (50 mg, 85 μmol) in $CHCl_3$ (5 mL) was stirred at room temperature for 20 h. After the completion of the reaction confirmed by ^{31}P NMR, the solvent was removed in vacuo. The product was recrystallized from $CHCl_3$/pentane to give colourless crystal of **C-HCl$_2$** (17 mg, 27 μmol, 32%). Single crystals suitable for X-ray crystallography were obtained by recrystallization from $CHCl_3$/pentane.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.72 (s, 2H, pyr-H3,H5), 3.81 (s, 3H, OCH_3), 3.72 (d vt, $^2J_{HH} = 16$ Hz, apparent $J = 2$ Hz, 2H, P–CH_2–pyr), 3.27 (d vt, $^2J_{HH} = 17$ Hz, apparent $J = 2$ Hz, 2H, P–CH_2–pyr), 3.14 (m, 2H, P–CH(CH_3)$_2$), 2.38 (m, 2H, P–CH(CH_3)$_2$), 1.49 (d vt, $^3J_{HH} = 8$ Hz, apparent $J = 8$ Hz, 6H, CH(CH_3)$_2$), 1.40 (d vt, $^3J_{HH} = 7$ Hz, apparent $J = 7$ Hz, 6H, CH(CH_3)$_2$), 1.35 (d vt, $^3J_{HH} = 8$ Hz, apparent $J = 8$ Hz,

6H, $CH(CH_3)_2$), 1.03 (d vt, $^3J_{HH} = 7$ Hz, apparent $J = 7$ Hz, 6H, $CH(CH_3)_2$), −22.50 (t, $^2J_{PH} = 12$ Hz, 1H, Ir–H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 166.1 (vt, apparent $J = 4$ Hz, pyr-C2,C6), 165.4 (s, pyr-C4), 106.5 (vt, apparent $J = 5$ Hz, pyr-C3,C5), 56.0 (s, OCH_3), 40.2 (vt, apparent $J = 12$ Hz, P–CH_2–pyr), 25.2 (vt, apparent $J = 14$ Hz, P–$CH(CH_3)_2$), 22.8 (vt, apparent $J = 15$ Hz, P–$CH(CH_3)_2$), 19.9 (m, $CH(CH_3)_2$), 18.7 (s, $CH(CH_3)_2$), 18.2 (s, $CH(CH_3)_2$), 18.1 (s, $CH(CH_3)_2$); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz): δ 28.81; IR (powder, cm^{-1}): ν_{Ir-H} 2214. HRMS(ESI) $[M - Cl]^+$ Calcd for $C_{20}H_{38}ClIrNOP_2$: 598.1746. Found: 598.1750.

Preparation of (*p*OMe-PNP)Ir (Cl)$_3$ (C-Cl$_3$). To a solution of hexachloroethane (52 mg, 0.22 mmol) in THF (1 mL) in a 20-mL Schlenk tube was added a solution of $[IrCl(coe)_2]_2$ (89 mg, 0.1 mmol) and *p*OMe-PNP ligand (**8**, 74 mg, 0.2 mmol) in THF (2 mL). After stirring for 1 day at 65 °C, the mixture was dried in vacuo. After the repetitive and exhaustive purification, (reprecipitation from CH_2Cl_2/hexane, extraction with benzene, reprecipitation from $CHCl_3$/benzene and then from CH_2ClCH_2Cl/benzene) a pale yellow powder of **C-Cl$_3$** was obtained (10 mg, 0.015 mmol, 7.5%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.84 (s, 2H, pyr-H3,H5), 3.88 (s, 3H, OCH_3), 3.75 (vt, apparent $J = 4$ Hz, 4H, P–CH_2–pyr), 3.16 (m, 4H, P–$CH(CH_3)_2$), 1.52 (d vt, $^3J_{HH} = 8$ Hz, apparent $J = 8$ Hz, 12H, $CH(CH_3)_2$), 1.43 (d vt, $^3J_{HH} = 7$ Hz, apparent $J = 7$ Hz, 12H, $CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 166.7 (s, pyr-C4), 166.0 (vt, apparent $J = 3$ Hz, pyr-C2,C6), 107.3 (vt, apparent $J = 5$ Hz, pyr-C3,C5), 56.1 (s, OCH_3), 39.4 (vt, apparent $J = 13$ Hz, P–CH_2–pyr), 23.1 (vt, apparent $J = 14$ Hz, P–$CH(CH_3)_2$), 19.6 (s, $CH(CH_3)_2$), 19.1 (s, $CH(CH_3)_2$); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 7.59; HRMS(ESI) $[M - 2Cl + H]^+$ Calcd for $C_{20}H_{38}ClIrNOP_2$: 598.1746. Found: 598.1739.

Mercury Poisoning Test for Hydrogenation of Carbon Dioxide. Catalyst **A-H$_3$** (20 µmol) was dissolved in THF (4.00 mL) and diluted to 100 µmol L^{-1}. To the 50 mL stainless autoclave equipped with a PTFE inner-tube and a small funnel, the solution of catalyst (100 µL), degassed aqueous KOH (1.00 M, 5.00 mL) and Hg (30 µL, 2.0 mmol) were charged and pressurized with CO_2 (2.5 MPa) and H_2 (2.5 MPa). The reaction mixture was stirred at 200 °C for 1.5 h. Yield of potassium formate was calculated to be 0.24 mmol (TON 24000) by ^{1}H NMR in D_2O with sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard. The activity is consistent with that without adding mercury (TON 24000).

Equilibrium between Dihydridoamidoiridium Complex B-H$_2$amido, H$_2$ and Trihydrodoiridium Complex B-H$_3$. To a solution of **B-H$_2$amido** (9.5 mg) in C_6D_6 (0.5 mL) in a screw-capped NMR tube, 1 atm of H_2 was introduced after freeze-thaw. After heating at 55 °C for 23 h, trihydrido complex **B-H$_3$** was observed by ^{1}H and ^{31}P NMR analysis with 80% conversion. Argon was then introduced by a freeze-thaw cycle. The NMR sample tube was heated at 55 °C for 22 h and 80 °C for 28 h. Disappearance of **B-H$_3$** and appearance of **B-H$_2$amido** were observed by ^{1}H and ^{31}P NMR analysis.

X-ray Crystallographic Data. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-1402670 for complex **A-HCl$_2$**, 1402671 for complex **B-H$_2$Cl**, 1402672 for complex **B-HCl$_2$** and 1402673 for complex **C-HCl$_2$**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

A part of this work was conducted in Research Hub for Advanced Nano Characterization, The University of Tokyo, supported by MEXT, Japan. The computations were performed using Research Centre for Computational Science, Okazaki, Japan.

Supporting Information

Experimental procedure, additional experimental results, detail for the X-ray structural analysis, and the detail for the theoretical calculations. This material is available on http://dx.doi.org/10.1246/bcsj.20150311.

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