

Hydrogenation of Carbon Dioxide with Organic Base by PC^{II}P-Ir Catalysts

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Supporting Information

ABSTRACT: Novel PC^{II}P-Ir^I monochloride complexes (1-Cl and 2-Cl) bearing a phosphine-carbene-phosphine pincer type ligand were synthesized. Reactions of 1-Cl with hexachloroethane, hydrogen chloride, and lithium triethylborohydride under a dihydrogen atmosphere afforded PC^{II}P-Ir^{III} trichloride (1-Cl₃), hydride dichloride (1-HCl₂), and trihydride (1-H₃) complexes, respectively. The strong electron-donating ability of carbene in PC^{II}P-Ir complexes was confirmed by X-ray crystallography and DFT calculations. Moreover, in complex 1-Cl, strong π backdonation from the iridium center to the carbene carbon was observed. Hydrogenation of CO2 with triethanolamine catalyzed by PC^{II}P-Ir complexes was investigated. The novel PC^{II}P-Ir complex 1-Cl exhibited a longer lifetime in comparison to the PNP-Ir^{III} complex 3-H₃: the turnover number of 1-Cl is



significantly higher than that of 3-H₃ (in 46 h, 1-Cl 230000 and 3-H₃ 54000).

INTRODUCTION

Formic acid is one of the most fundamental chemical products, which is used as a preservative agent in livestock feed, for leather tanning, and for dyeing textiles.¹ The global demand of formic acid was 579000 tons/year in 2013 and average annual growth of consumption in the world will continue at 3.7% until 2020.^{2,3} Most of the industrial production relies upon the carbonylation of methanol with CO and successive hydrolysis.¹ Hydrogenation of CO₂ has attracted great attention and has been developed in industry as an alternative route for the production of formic acid because of the abundance and lessened toxicity of CO₂ in comparison to CO.^{3,4} In addition to the high demand of formic acid as a basic chemical, its high potential as a hydrogen-storage material has also motivated the increasing importance of catalyst development.¹ Along with one hundred years of history for catalytic CO₂ hydrogenation,⁵ especially since the first report with a well-defined complex catalyst by Inoue in 1976,⁶ numerous researchers have focused their attention on the development of active and robust homogeneous and heterogeneous catalysts for hydrogenation of CO_2 .^{7–9} Until now, various transition-metal homogeneous catalysts, such as Ir,^{10–12} Rh,¹³ Ru,^{14,15} Fe,¹⁶ Ni,¹⁷ Co,¹⁸ etc.,¹⁹ have been developed for highly active CO₂ hydrogenation. In almost all the precedents, bases have been employed in order to accelerate the reaction and make it thermodynamically favorable.^{7,20,22a}

In 2009, we reported that a PNP-Ir^{III} pincer-type complex showed the highest catalytic turnover number (TON), 3500000, in the presence of potassium hydroxide.¹¹ From the viewpoint of industrial application, weak organic bases have an advantage in the purification process. Namely, formic acid can be isolated via simple distillation from the produced salts with a weak organic base, while with strong inorganic base, neutralization is inevitable for formic acid production.²² Moreover, the amine after separation from formic acid salt by distillation can be recycled. The PNP-Ir catalyst, however, showed a much lower turnover frequency (TOF 14000 h^{-1} in 2 h) and turnover number (29000) with trialkylamine instead of hydroxide base.²³ Other representative examples where catalytic hydrogenation of CO₂ was conducted under organic base conditions are summarized in Scheme 1A. Jessop et al. reported a ruthenium-based catalyst (TOF 95000 h^{-1} , 0.3 h) with triethylamine.^{14b} Pidko and co-workers reported a remarkably high TOF by PNP-Ru catalyst in the presence of DBU (1100000 h⁻¹, ~ 2 min).^{15a} However, there still remains a strong demand for the development of a highly active and robust catalyst in CO₂ hydrogenation with organic bases.

In 2016, we found that an electron-rich ligand improved the catalytic activity under organic base conditions (Scheme 1B).²

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Scheme 1. (A) Representative Examples for Hydrogenation of CO_2 with Organic Bases, (B) Electron-Donating Effect for Hydrogenation of CO_2 Catalyzed by PNP-pincer-Ir Complexes and Cationic Rate-Determining Transition State in Hydrogenation of CO_2 by PNP-pincer-Ir Complex, and (C) Hydrogenation of CO_2 by PC^{II}P-pincer-Ir Complexes (This Work)



The TON was 1.5 times higher with a 4-methoxy-substituted PNP iridium complex than with unsubstituted PNP-Ir (TOF 12000 and 8500 h⁻¹, respectively, in 2 h), presumably because the cationic key transition state suggested by theoretical calculations was stabilized by an electron-donating methoxy group (Scheme 1B).^{21,23} In the last four decades, on the other hand, many variations of PXP pincer-type tridentate ligands have been developed, aiming at stable coordination of a strongly electron-donating X molety such as anionic $C^{-,25}$ N^{-,26} B^{-,27} and Si⁻²⁸ and neutral P,²⁹ N,³⁰ C(II),^{31,32} Si(II),³³ etc.³⁴ Among them, we focused our attention on a PC^{II}P skeleton bearing carbene central donor. A PC^{II}P pincer ligand was shown in 2017 to exhibit higher electron donation stemming from its higher σ -donating ability in dinitrogen reduction catalyzed by PC^{II}P molybdenum complexes.³⁵ Thus, we envisioned that the introduction of a more electrondonating moiety, a carbene donor, into a tridentate pincer skeleton would lead to a dramatic improvement in the catalytic performance in CO₂ hydrogenation. In this report, we developed PC^{II}P-Ir complexes bearing a carbene as a neutral donor at the center of a pincer-type tridentate ligand. In the investigation of hydrogenation of CO₂ with triethanolamine catalyzed by PC^{II}P-Ir complexes, an improved turnover number was achieved by PC^{II}P-Ir complexes in comparison to a pyridine-based PNP pincer iridium complex.

RESULTS AND DISCUSSION

Synthesis and Characterization of PC^{II}P-Ir^I and -Ir^{III} Complexes. The novel PC^{II}P-Ir monochloride complexes 1-Cl and 2-Cl were prepared according to Scheme 2a,b. Complexation of the PCP ligand precursors 1,3-bis(di-*tert*- Scheme 2. Synthesis of (a) 1-Cl, (b) 2-Cl, (c) 1-HCl₂, 1-Cl₃, and 1-H₃, and (d) 2-HCl₂



butylphosphinomethyl)benzimidazolium hexafluorophosphate (1-H⁺) and 1,3-bis(2-(di-tert-butylphosphino)ethyl)imidazolium chloride $(2-H^+)$ with $[IrCl(coe)_2]_2$ and [IrCl- $(C_2H_4)_2]_2$ proceeded cleanly to afford the tetracoordinated iridium(I) chlorides 1-Cl and 2-Cl, respectively.³⁶ The formation of a stable iridium(I) chloride complex is in sharp contrast to a PNP-Ir monochloride complex, which could not be isolated because of the immediate release of hydrogen chloride to afford a dearomatized PN(amide)P Ir complex.²³ The structures of 1-Cl and 2-Cl were unambiguously characterized by X-ray single-crystal diffraction analyses (Figure 1). Complexes 1-Cl and 2-Cl both have square-planar coordination geometries. Complex 1-Cl has almost the same Ir-Cl bond length as complex 2-Cl. In contrast, complex 1-Cl showed a significantly shorter Ir-carbene bond length than 2-Cl by 0.06 Å (1-Cl, 1.889(5) Å; 2-Cl, 1.959(4)/1.943(5)/ 1.957(4) $Å^{37}$). This shorter Ir–C bond in 1-Cl than in 2-Cl is probably because of the stronger π back-donation from Ir to the carbene carbon in 1-Cl. In 1-Cl, filled d orbital on iridium is effectively overlapped with a vacant p orbital on carbene, which can be confirmed in the X-ray structure as a smaller torsion angle between the NHC plane and Ir-coordination plane in 1-Cl than in 2-Cl (1-Cl, 2.55°; 2-Cl, 44.2°; see also the NBO analysis section).

Previously, we reported that the number of chloride ligands and hydride ligands on the iridium(III) catalyst precursor



Figure 1. Molecular structures and structural parameters of complexes 1-Cl (left) and 2-Cl (right). Thermal ellipsoids are drawn with 50% probability. Hydrogens and cocrystallized solvents are omitted for clarity.

strongly affected the turnover number in PNP-Ir^{III}-catalyzed reactions.²⁴ Therefore, we synthesized PCP-Ir^{III} complexes with different numbers of chloride ligand or hydride ligand on iridium: complexes 1-HCl₂, 1-Cl₃, 1-H₃, and 2-HCl₂ were synthesized from PCP-Ir^I complexes 1-Cl and 2-Cl as shown in Scheme 2c,d. Oxidative addition of HCl to complexes 1-Cl and 2-Cl afforded Ir(III) hydride dichloride complexes 1-HCl₂ and 2-HCl₂ as the sole reaction products. 1-HCl₂ was stable enough to be fully characterized, while 2-HCl₂ gradually converted to a hardly soluble unknown complex upon standing in THF solution. Both 1-HCl₂ and 2-HCl₂ were successfully characterized by X-ray crystallography. X-ray structures of complexes 1-HCl₂ and 2-HCl₂ and the previously reported PNP-Ir hydride dichloride complex 3-HCl₂ are shown in Figure 2 with their structural parameters. All of these three complexes have a hydride ligand at the coordination site cis to the carbene or pyridine donor. Complexes 1-HCl₂ and 2-HCl₂ show significantly longer Ir-Cl bond lengths in comparison to 3-HCl₂, reflecting the stronger σ donation of carbene ligands in comparison to pyridine (2.4602(9) , 2.4408(16)/ 2.4451(17), 37 and 2.300(3)/2.327(2) Å 37 for 1-HCl2, 2-HCl₂, and 3-HCl₂ respectively). While, upon oxidative

addition of HCl, the tilt angle between the NHC plane and Ir coordination plane was only slightly changed from 44.2° in 2-Cl to 42.0° in 2-HCl₂, 1-HCl₂ exhibited a significantly larger tilt angle in comparison to 1-Cl (2.55° in 1-Cl to 16.1° in 1-HCl₂). This is presumably because the strong π back-bonding interaction in 1-Cl is greatly weakened on oxidation of Ir(I) to Ir(III) (see also the NBO analysis section). The trichloride complex 1-Cl₃ and iridium trihydride complex 1-H₃ were also successfully synthesized by treatment of 1-Cl with hexachloroethane or with LiHBEt₃ under 2.5 MPa of dihydrogen, respectively.³⁸ In contrast to the clean formation of all these iridium(III) complexes, 1-HCl₂, 1-Cl₃, and 1-H₃, the attempted oxidative addition of dihydrogen to 1-Cl resulted in a low conversion of 3.3% (see the Supporting Information for details).

Theoretical Studies on Comparison of PCP and PNP Complexes. We employed theoretical calculations using DFT and NBO analysis for complexes 1-Cl, 1-H₂Cl, 3-Cl, 3-H₂Cl, and 2-Cl in order to estimate the strength of σ donation, π back-donation, and electron density on the iridium in PCP-Ir and PNP-Ir complexes. Calculations were performed with the Gaussian 09 package at the M06L level using SDD basis sets (and associated effective core potentials) for transition metals and 6-311+G^{**} basis sets for all light elements in the gas phase at 298.15 K. First, geometry optimization and free energy calculations revealed that oxidative addition of dihydrogen to 1-Cl is endergonic by 13 kcal/mol while that to PNP-Ir-Cl (3-Cl) is exergonic by -17 kcal/mol (Scheme 3), which is in







Figure 2. X-ray structures and structural comparison among 1-HCl₂, 2-HCl₂, and 3-HCl₂. Thermal ellipsoids are drawn with 50% probability. Cocrystallized solvents are omitted for clarity.

good agreement with the observed low conversion of oxidative addition of dihydrogen to 1-Cl (see Schemes S1 and S2 in the Supporting Information). This strong preference of low oxidation state with PCP ligand could be attributed to the stronger stabilization of occupied Ir d_{yz} and d_{z}^2 orbitals by back-donation to the vacant p orbital on the carbene carbon in the PC^{II}P complex (1-Cl), which is suggested by NBO second-order perturbation analyses (the results are summarized in Table 1). Both PCP-Ir complexes show much stronger π back-

Table 1. Results of Theoretical Calculations

	1-Cl	1-H ₂ Cl	3-Cl	3-H ₂ Cl	2-Cl
back-donation ^a (kcal/mol)	137	39.0	12.2	2.13	95.3
torsion angle (deg) (NCN and PCP, CNC and PNP)	3.37	10.6	15.4	12.9	40.8
Ir–carbene or –N bond length (Å)	1.89685	2.02702	2.03328	2.20021	1.95029
Ir-Cl or -H (trans to carbene or N) bond length (Å)	2.46882	1.66154	2.39841	1.59877	2.48858
NBO charge	-0.597	-1.09	-0.532	-0.957	-0.619

"Electron transfer from the d orbital on the metal to the empty p orbital on the ligand:



donation from iridium d_{yz} and d_{z}^{2} orbitals to a carbene p-type orbital in comparison to that of a PNP-Ir complex to a pyridine π^* orbital (stabilization energy: 137 kcal/mol in 1-Cl, 95.3 kcal/mol in 2-Cl, and 12.2 kcal/mol in 3-Cl). In comparison to imidazolylidene complex 2-Cl, benzo-fused imidazolylidene complex 1-Cl displayed a much stronger π back-bonding interaction, probably because of the larger overlap of iridium d_{yz} and d_{z} orbitals and the carbene p orbital accompanied by smaller torsion between the NHC plane and Ir coordination plane.³⁵ Upon oxidation to Ir(III) $(1-H_2Cl)$, the torsion angle in 1-Cl was significantly increased $(3.37^{\circ} \text{ to } 10.6^{\circ} \text{ in the}$ calculated structure) along with a decrease in π back-donation from the iridium center, which is the same trend as oxidative addition of HCl to 1-Cl observed experimentally (torsion angle 2.55° in 1-Cl to 16.1° in 1-HCl₂) (Figures 1 and 2). The bond distance between Ir and carbene in 1-Cl is shorter than that in 2-Cl (1-Cl, 1.89685 Å; 2-Cl, 1.95029 Å). These calculated bond lengths are consistent with experimental data (Figure 1 and Table 1). PC^{II}P-Ir complexes 1-Cl and 2-Cl have longer Ir-Cl bonds in comparison to the corresponding PNP-Ir complex 3-Cl (1-Cl, 2.46882 Å; 2-Cl, 2.48858 Å; 3-Cl, 2.39841 Å). This implies that the carbene in the PCP-Ir complex has strong electron-donating ability. Significantly larger negative NBO charges on the iridium centers in 1-Cl and $1-H_2Cl$ in comparison to 3-Cl and $3-H_2Cl$ (1-Cl, -0.597; 1-H₂Cl, -1.09; 3-Cl, -0.532; 3-H₂Cl, -0.957) also support the stronger electron donation from the carbene carbon to the iridium center in comparison to that from pyridine nitrogen in both Ir(I) and Ir(III) states.

Catalytic Hydrogenation of Carbon Dioxide. The hydrogenation of carbon dioxide catalyzed by PCP-Ir complexes 1-Cl, 2-Cl, 1-HCl₂, and 1-Cl₃ was examined by using triethanolamine as a base in water at 120 °C (Table 2).³⁶

Table 2. Catalytic Hydrogenation of CO₂ by Ir Complexes

		1.	Ir cat. (0.010 µmol) 0 M N(CH₂CH₂OH)₃ aq. (, (5.0 mL)	⊖ ⊕_	
H ₂ + CO ₂		CO ₂ — 1) IPa	THF (0.1 mL), 120 °C, time HCOO HNR ₃			
entry	Ir cat.	time (h)	TON ^a (± standard error)	TOF (h ⁻¹)	−	
1	1-CI	2	8,700 ±360	4,400		
2	2-CI	2	3,500 ±580	1,800	Ĺ	
3	1-HCl ₂	2	16,000 ±2,100	7,900	3-Ha	
4	1-Cl ₃	2	30,000 ±4,000	15,000	0 113	
5	3-H ₃	2	9,800 ±2,300	4,900		
6	1-CI	46	230,000 ±44,000	5,000		
7	2-CI	46	62,000 ±7,000	1,300		
8	1-Cl ₃	46	130,000 ±5,000	2,700		
9	$3-H_3$	46	54,000 ±8,000	1,200		
10 ^b	1-CI	13	3,600 -	280		

^{ar}TON based on ¹H NMR analysis using sodium 3-(trimethylsilyl)-1propanesulfonate as an internal standard. ^bTrioctylamine (5.0 mmol), THF (2.5 mL), and H₂O (2.5 mL) were used.

Each entry (other than entry 10) shows the average value of more than two trials, and standard errors are given after the turnover numbers. The catalytic reaction was performed with complete exclusion of any metal impurities or carbon monoxide for better reproducibility (see section 3 in the Supporting Information for experimental details). Complex 1-Cl showed a higher TON in comparison to complex 2-Cl in 2 h (entries 1 and 2, TON: 1-Cl 8700, 2-Cl 3500). While further investigation is required to clarify the reason for the lower activity of 2-Cl, the decomposition to an unknown insoluble complex, which was observed in the oxidative addition of HCl to 2-Cl, could have suppressed the catalytic activity. When complexes bearing a $PC^{II}P$ ligand (1) were employed, the increase of chloride ligands on iridium resulted in a higher TON to achieve 30000 turnovers in 2 h with 1-Cl₃ (compare entries 1, 3, and 4). The effect of the chloride ligand on catalytic activity was also observed in our previous research,²⁴ although the reason is still unclear at this moment. On comparison of these results with PNP-Ir trihydride complex 3-H₃, PC^{II}P complexes 1-HCl₂ and 1-Cl₃ achieved significantly higher TON than $3-H_3$ (entries 1 and 3-5). In 46 h, the highest turnover number of 230000 was accomplished by 1-Cl among the examined complexes (entries 6-9). Although significant deceleration was observed, 2-Cl and 1-Cl₃ still achieved higher TONs (62000 and 130000, respectively, in entries 7 and 8) than 3-H₃ in 46 h (entry 9, TON 54000). This result indicates that PCP-Ir complexes are more robust than PNP-Ir complexes and, among them, complex 1-Cl is the most robust, enough under these reaction conditions to keep its activity over 46 h. The significant increase in the reaction rate along with the reaction progress using 1-Cl as a catalyst (TOF 4400 in the initial 2 h to 5000 in 46 h) suggests that the active Ir(III) species was gradually generated in situ, presumably via the slow oxidative addition of dihydrogen. In addition to triethanolamine, trioctylamine was also examined as a base to show that complex 1-Cl is also active in CO_2 hydrogenation with trioctylamine, albeit with lower activity (entry 10). Although the initial turnover frequency is not comparable to

that of the ruthenium-catalyzed system reported by Pidko and co-workers, complex **1-Cl** exhibited one of the highest catalytic turnover numbers (230000) in the reported hydrogenation of CO_2 with organic bases (e.g., Pidko's PNP-ruthenium catalyst (TOF 1100000 h⁻¹ in 2 min and TON 200000)^{15a} or Jessop's RuCl(OAc)(PMe₃)₄ (TOF 95000 h⁻¹ in 0.3 h and TON 32000)^{14b}).

CONCLUSION

In conclusion, $PC^{II}P$ -Ir complexes bearing a tridentate P-C(carbene)-P ligand were synthesized and used for catalytic hydrogenation of carbon dioxide with organic bases. The stronger electron-donating ability of the $PC^{II}P$ ligand in comparison to the PNP ligand was confirmed by X-ray crystallography and theoretical calculations. DFT calculations and NBO analysis revealed that strong π back-donation as well as σ donation exists in PCP-iridium complexes and made the catalyst robust. By use of the newly synthesized $PC^{II}P$ -Ir^I monochloride complex 1-Cl, a catalytic turnover of 230000 was achieved. The improved reactivity in comparison to the PNP-Ir system could be attributed to the stabilization of the cationic key transition state by the higher electron-donating nature of the $PC^{II}P$ ligand.

EXPERIMENTAL SECTION

General Procedures. All manipulations involving air- and moisture-sensitive compounds were carried out in an argon-filled glovebox or using standard Schlenk techniques under purified argon or nitrogen by passing through a hot column packed with BASF catalyst R3-11. All of the organic solvents used for reactions were purified by the method of Pangborn et al.³⁹ Most of the reagents were used without further purification unless otherwise specified. NMR spectra were recorded on 400 and 500 MHz spectrometers (JEOL JNM-ECS400 or BRUKER Ascend500). Chemical shifts are reported in ppm relative to the residual protiated solvent for ${}^{1}H$ (C₆D₆, 7.16 ppm; CDCl₃, 7.26 ppm; tetrahydrofuran-d₈, 1.72 ppm), deuterated solvent for ¹³C (C₆D₆, 128.06 ppm; CDCl₃, 77.16 ppm; tetrahydrofuran-d₈, 25.31 ppm), and external 85% H₃PO₄ for ³¹P nuclei. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, vt = virtual triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers and class of carbon (CH₃ = primary carbon, CH₂ = secondary carbon, CH = tertiary carbon, C = quaternary carbon, carbene). IR spectra were recorded on a Shimadzu FTIR-8400 instrument. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, Graduate School of Science, The University of Tokyo, or by the One-stop Sharing Facility Center for Future Drug Discoveries, Graduate School of Pharmaceutical Sciences, The University of Tokyo. X-ray crystallographic analyses were performed on a Rigaku Varimax with a Saturn diffractometer. The following compounds were used as received: triethanolamine (Kanto Chemical Co. Inc. (Kanto)), potassium bis(trimethylsilyl)amide (Aldrich), 4.0 M HCl in dioxane (Aldrich), hexachloroethane (Tokyo Chemical Industry Co. Ltd. (TCI)), lithium triethylborohydride (Kanto). The following compounds were synthesized according to the literature procedures: bis(cyclooctene)chloridoiridium dimer,^{40a} bis(ethylene)chloridoiridium dimer,40b 1,3-bis(di-tert-butylphosphinomethyl)benzimidazolium hexafluorophosphate (1-H⁺),³⁵ 1,3-bis(2-(di-tertbutylphosphino)ethyl)imidazolium chloride (2-H+).38

Standard Procedure for Hydrogenation of Carbon Dioxide. The catalyst (20 μ mol) was dissolved in THF (10.0 mL) and diluted to 0.10 μ mol/mL. In the 50 mL stainless autoclave equipped with a glass liner, solutions of the catalyst (100 μ L, 0.010 μ mol) and degassed aqueous triethanolamine (1.00 M, 5.00 mL) were charged, and the autoclave was pressurized with CO₂ (2.5 MPa) and H₂ (2.5 MPa). The reaction mixture was stirred at 120 °C for an appropriate time. The yield of ammonium formate was determined by $^1\rm H$ NMR in $\rm D_2O$ with sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard.

Preparation of [1,3-Bis(di-*tert***-butylphosphinomethyl**- $\kappa P,P'$ **)benzimidazol-2-ylidene-\kappa C]chloridoiridium (1-Cl).** To a mixed solid of 1,3-bis(di-*tert*-butylphosphinomethyl)benzimidazolium hexafluorophosphate (425 μ mol, 247 mg) and potassium bis(trimethylsilyl)amide (553 μ mol, 110 mg) was added toluene (5.0 mL), and the resulting suspension was stirred for 2 h at room temperature. The insoluble salt that formed was filtered off through a pad of Celite, and the solvent was removed under reduced pressure. To a solution of the residual solid in THF (5.0 mL) was added bis(cyclooctene)chloridoiridium dimer (212 μ mol, 190 mg) in THF (5.0 mL). The reaction mixture changed from dark yellow to yellow during the following 12 h with vigorous stirring at room temperature. After the reaction, the solvent was removed under vacuum. The residue was recrystallized from THF/pentane to afford the desired complex 1-Cl as yellow crystals (238 mg, 85% yield).

¹Ĥ NMR (THF- d_8 , 400 MHz): δ 1.45 (vt, apparent J = 6.6 Hz, 36H), 3.83 (vt, apparent J = 2.3 Hz, 4H), 6.99 (dd, J = 5.8 Hz, 3.1 Hz, 2H), 7.12 (dd, J = 5.7 Hz, 3.2 Hz, 2H). ³¹P{¹H} NMR (THF- d_8 , 162 MHz): δ 77.9. ¹³C NMR (THF- d_8 , 126 MHz): δ 29.9 (vt, apparent $J_{CP} = 3.2$ Hz, CH₃), 36.9 (vt, apparent $J_{CP} = 9.1$ Hz, C), 41.8 (vt, apparent $J_{CP} = 13.2$ Hz, CH₂), 109.1 (s, CH), 122.0 (s, CH), 136.3 (vt, apparent $J_{CP} = 4.5$ Hz, C), 187.2 (t, $J_{CP} = 5.9$ Hz, carbene). Anal. Calcd for C₂₅H₄₄N₂P₂ClIr: C, 45.34; H, 6.70; N, 4.23. Found: C, 45.58; H, 6.58; N, 4.26.

Preparation of [1,3-Bis(di-*tert***-butylphosphinoethyl**-*κP*,*P***)imidazolylidene**-*κ***C]chloridoiridium (2-Cl).** To a mixed solid of 1,3-bis(2-(di-*tert*-butylphosphino)ethyl)imidazolium chloride (103 µmol, 46.3 mg) and potassium bis(trimethylsilyl)amide (124 µmol, 24.7 mg) was added toluene (3.0 mL), and the resulting suspension was stirred for 2 h at room temperature. The insoluble salt that formed was filtered off through Celite. The solvent was removed under reduced pressure, and to a solution of the residual solid in THF (2.0 mL) was added bis(ethylene)chloridoiridium dimer (28.9 µmol, 16.4 mg) in THF (5.0 mL). The reaction mixture changed from colorless to orange during the following 24 h with vigorous stirring. After the reaction, the solvent was removed under vacuum. The residue was recrystallized from diethyl ether at −35 °C to afford the desired complex 2-Cl as yellow crystals (53.7 mg, 82% yield).

¹H NMR (C_6D_6 , 400 MHz): δ 1.29 (br, 4H), 1.48 (vt, apparent J = 6.1 Hz, 36H), 3.42 (br, 4H), 5.92 (s, 2H). ³¹P{¹H} NMR (C_6D_6 , 162 MHz): δ 35.2. ¹³C NMR (C_6D_6 , 126 MHz): δ 17.9 (vt, apparent $J_{CP} = 3.2$ Hz, CH₂), 31.0 (s, CH₃), 36.5 (vt, apparent $J_{CP} = 10$ Hz, C), 49.2 (vt, apparent $J_{CP} = 3.2$ Hz, CH₂), 116.6 (s, CH), 157.9 (t, $J_{CP} = 10$ Hz, carbene). Anal. Calcd for C₂₃H₄₆N₂P₂ClIr: C, 43.15; H, 7.24; N, 4.38. Found: C, 43.23; H, 6.98; N, 4.12.

Preparation of [1,3-Bis(di-*tert***-butylphosphinomethyl**-*κ***P**,**P')benzimidazol-2-ylidene-***κ***C]hydridodichloridoiridium (1-HCl₂).** To a solution of 1-Cl (102 μmol, 67.6 mg) in THF (1.0 mL) was added 4.0 M HCl in dioxane (4.0 mmol, 1.0 mL), and the reaction mixture was allowed to stand for 10 s at room temperature. The desired complex 1-HCl₂ was reprecipitated from THF/pentane as a colorless solid (34.6 mg, 49% yield).

¹H NMR (CDCl₃, 400 MHz): δ –20.0 (t, *J*_{HP} = 14 Hz, 1H), 1.35 (vt, apparent *J* = 6.7 Hz, 18H), 1.66 (vt, apparent *J* = 7.1 Hz, 18H), 4.08 (dvt, *J*_{HH} = 13 Hz, apparent *J*_{PH} = 2.5 Hz, 2H), 4.37 (d, *J*_{HH} = 13 Hz, 2H), 7.24 (dd, *J* = 5.9 Hz, 3.2 Hz, 2H), 7.31 (dd, *J* = 5.7 Hz, 3.1 Hz, 2H). ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ 53.0. ¹³C NMR (CDCl₃, 126 MHz): δ 29.4 (s, CH₃), 30.6 (s, CH₃), 37.2 (vt, apparent *J*_{CP} = 12 Hz, C), 39.9 (vt, apparent *J*_{CP} = 7.7 Hz, C), 43.0 (vt, apparent *J*_{CP} = 11.4 Hz, CH₂), 110.7 (s, CH), 123.5 (s, CH), 134.1 (vt, apparent *J*_{CP} = 3.2 Hz, C), 179.2 (s, carbene). IR (ATR, cm⁻¹) ν _{tr-H} 2303. Anal. Calcd for C₂₉H₅₃N₂OP₂Cl₂Ir (1-HCl₂·THF): C, 45.19; H, 6.93; N, 3.63. Found: C, 44.96; H, 6.94; N, 3.54.

Preparation of [1,3-Bis(di-tert-butylphosphinomethyl- $\kappa P,P'$)benzimidazol-2-ylidene- κC]trichloridoiridium (1-Cl₃). To a solution of 1-Cl (106 μ mol, 70.2 mg) in THF (5 mL) was added hexachloroethane (162 μ mol, 38.4 mg). After the mixture was stirred at room temperature for 24 h, the solvent was removed under reduced pressure. The desired complex $1-Cl_3$ was reprecipitated from THF/pentane as a yellow solid (46.9 mg, 60% yield).

¹H NMR (CDCl₃, 400 MHz): δ 1.53 (vt, apparent J = 6.9 Hz, 36H), 4.57 (s, 4H), 7.32 (dd, J = 5.7 Hz, 3.1 Hz, 2H), 7.43 (dd, J = 5.9 Hz, 3.2 Hz, 2H). ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ 27.4. ¹³C NMR (THF- d_8 , 126 MHz): δ 31.5 (s, CH₃), 40.6 (vt, apparent $J_{CP} = 6.8$ Hz, C), 44.2 (vt, apparent $J_{CP} = 11.8$ Hz, CH₂), 111.6 (s, CH), 124.0 (s, CH), 135.2 (vt, apparent $J_{CP} = 2.7$ Hz, C), 172.4 (s, carbene). Anal. Calcd for C₂₉H₅₂N₂OP₂Cl₃Ir (1-Cl₃·THF): C, 43.26; H, 6.51; N, 3.48. Found: C, 43.36; H, 6.54; N, 3.40.

Preparation of [1,3-Bis(di-tert-butylphosphinomethyl*κP,P'*)**benzimidazol-2-ylidene-***κ***C**]**trihydridoiridium (1-H₃).** To a solution of 1-Cl (73.1 μ mol, 48.5 mg) in THF (5 mL) was added lithium triethylborohydride (0.99 M THF solution, 1.43 mmol, 1.44 mL), and the reaction mixture was pressurized with 2.5 MPa of H₂ in a 50 mL stainless autoclave. After the mixture was stirred at 60 °C for 2.5 days, the solvent was removed under vacuum. The product was extracted with Et₂O from the residual solid and filtered through a pad of Celite. After the solvent was removed under reduced pressure, the residue was dissolved in THF and passed through a pad of silica gel. Recrystallization from diethyl ether at -35 °C afforded the desired complex 1-H₃ as red crystasl (20.0 mg). In spite of the repetitive recrystallizations, 1-H₃ could not be isolated, probably due to facile decomposition to an unknown product in solution (see spectroscopic analyses in the Supporting Information).

Preparation of [1,3-Bis(di-tert-butylphosphinoethyl-κ*P*,*P*')imidazolylidene-κC]hydridedichloridoiridium (2-HCl₂). To a solution of 2-Cl (25.3 μmol, 16.2 mg) in THF (1.0 mL) was added 4.0 M HCl in dioxane (6.0 mmol, 1.5 mL). Reprecipitation from pentane at -30 °C afforded a white solid. After removal of solvent, recrystallization from CHCl₃/pentane under a hydrogen chloride atmosphere afforded a tiny amount of crystals which was suitable for single-crystal X-ray crystallographic analysis. Because of its instability, satisfactory data for ¹H NMR, ¹³C NMR, or elemental analysis could not be obtained.

³¹P{¹H} NMR (C₆D₆, 162 MHz): δ 11.2.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00377.

Experimental details, spectroscopic data for the complexes, details of the theoretical calculations, additional experimental data, and X-ray diffraction analyses (PDF) Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1841924–1841928 and 1841930 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(36) We attempted to synthesize PCP-Ir complexes which had ⁱPr groups on phosphorus atoms (ⁱPr-PCP-Ir), because in catalytic hydrogenation of CO₂ by PNP-Ir complexes, the complex that had ⁱPr groups on phosphorus atoms exhibited a higher turnover number in comparison to the complex that had ⁱBu groups on phosphorus atoms. However, unfortunately, we were unable to isolate ⁱPr-PCP-Ir complex. Instead, we evaluated the catalytic activity by using ⁱBu-PCP-Ir complexes.

(37) When one crystal lattice consists of multiple inequivalent complexes, every bond distance is shown.

(38) The trihydride complex decomposed to an unknown complex in a solution state although no reductive elimination of dihydrogen was observed, preventing further investigation in catalytic reaction. Details are given in the Supporting Information.

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