Preferential Geometry and Reactivity of Neutral Iridium(III) and Rhodium(III) Complexes Bearing a Flexible Heterochelate PN Ligand (PN = *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2)

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Reactions of $[IrCl(coe)_2]_2$ (coe = cyclooctene) with 1 equiv of the PN ligand (PN = *o*-$Ph_2PC_6H_4CH_2$-$OCH_2C_5H_4N$-2) in the presence of several phosphines or pyridine (1 equiv) at room temperature afforded a neutral iridium(III) hydride complex, (PCN-κ^3*P,C,N*)Ir(H)(Cl)(*L*) (PCN = $Ph_2PC_6H_4CHOCH_2C_5H_4N$) [*L* = PPh_3 (**1a**), PCy_3 (**1b**), PBu_3 (**1c**), $PMePh_2$ (**1d**), Py (**1e**)] in good isolated yield. The PCN ligand is coordinated in a meridional manner, which was confirmed by spectral analyses and X-ray analysis of **1a**. The related rhodium(III) hydride complex (PCN-κ^3*P,C,N*)Rh(H)(Cl)(*L*) (PCN = $Ph_2PC_6H_4CHOCH_2C_5H_4N$) [*L* = PPh_3 (**4a**), PCy_3 (**4b**)] was also prepared from the reactions of $[RhCl(coe)_2]_2$ with 1 equiv of the PN ligand in the presence of 1 equiv of PPh_3 or PCy_3. The structure of **4a** and **4b** was determined by spectral analyses and X-ray analysis of **4a**. In contrast to the iridium complexes, the PCN ligand in the rhodium-(III) complexes coordinated to the metal center in a facial manner. A ligand exchange reaction of the PPh_3 iridium(III) complex **1a** with PCy_3 did not proceed well (20% conversion), while a similar reaction of the PPh_3 rhodium(III) complex **4a** with PCy_3 afforded the PCy_3 complex **4b** quantitatively. We examined the ligand exchange reactions of the iridium(III) and rhodium(III) complexes with various phosphines to explain the different reactivities. Using Tolman's parameter, we demonstrated that the ligand exchange reaction in the iridium(III) complexes bearing the meridional-coordinated PCN ligand is controlled by the steric factor of the phosphines and the ligand exchange reaction in the rhodium(III) complexes bearing the facial-coordinated PCN ligand is controlled by their electronic factors. The meridional coordination of the PCN ligand makes the environment around the iridium center sensitive to the steric nature due to the steric repulsion between the diphenyl group in the PCN ligand and the phosphines. The facial coordination of the PCN ligand decreases their repulsion, and reactivity of the metal center depends on the basicity of the phosphines.

Introduction

Hybrid chelate ligands containing mixed functionalities connected by an appropriate spacer are widely used in both organic chemistry as an optically active chiral ligand for highly selective asymmetric reactions and in coordination chemistry as an auxiliary ligand for the isolation of interesting and important metal complexes.[1−18] In particular, a special class of these ligands with substitutionally inert and labile parts is generally called a hemilabile ligand, and the chemistry of transition metal complexes bearing these ligands has received considerable attention. Several hemilabile ligands have been synthesized and complexed to various metal centers to construct systems mediated or catalyzed by complexes focused on opening a coordination site by dissociation of the weaker functional group for small molecule activation and closing it by recoordination for the stabilization of reactive and unsaturated metal species. For example, Braunstein and co-workers reported that Pd complexes bearing the tridentate NPN ligand and showing reactivity at the Pd center are controlled by the hemilability of the ligand.[7]

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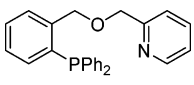
Chart 1



PN Ligand

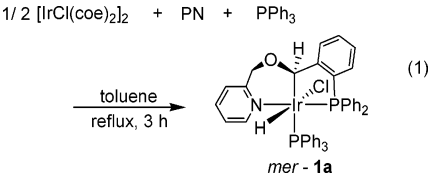
Transition metal complexes bearing hybrid chelate ligands have also been used for bond activation chemistry. Andersson reported that P−O heterochelate ligands undergo C−H bond activation in the benzylic position.[19−21] Tejel described that P−N heterochelate ligands undergo C(sp^3)−H activation reactions.[22,23] Milstein reported that iridium and rhodium complexes bearing the PCN pincer ligands control whether the C−H or C−C bond is activated.[13−16]

Another interesting feature inherent to hemilabile ligands is their flexibility. A flexible ligand can change its coordination pattern to the metal center due to a subtle modification of the reaction conditions and transform the structure of the complex. If the complex before and after the transformation has a unique and characteristic reactivity, the complex can work as a multifunctional catalyst. It is a challenging project, however, to construct systems in which the reactivity of complexes bearing the same ligands is dramatically changed.

In our laboratories, we have studied the chemistry of hemilabile ligands and designed a heterochelate PN hybrid ligand (PN = *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2) (Chart 1). We demonstrated that the PN ligand has the flexibility to act as a P−N bidentate, a P−O−N tridentate, and a P−C−N tridentate ligand.[24−31] One characteristic behavior of this flexibility is that both iridium(I) and iridium(III) cationic complexes before and after an intermolecular C−H bond activation can be isolated as a result of changing the coordination mode of the PN ligand.[28] Subsequent studies of our hybrid chelate ligand demonstrated the stereoselective activation of a prochiral C−H bond by iridium complexes bearing the optically active PN ligand.[31] The selectivity was controlled by a difference in the thermodynamic stability of the iridium(III) hydride complexes obtained by repeated and reversible C−H bond activation due to the flexibility of the PN ligand. Compared to the cationic system of iridium complexes bearing the PN ligand, the chemistry of a neutral complex bearing the same PN ligand has not been explored because the polymeric species $[(PN)IrCl(cod)]_n$ obtained by the reaction of $[IrCl(cod)]_2$ with the PN ligand could not cleanly induce the intramolecular C−H bond activation. Herein, our main objective was to prepare the first neutral iridium(III) complexes bearing our PN ligand by intramolecular C−H bond activation as well as neutral rhodium(III) complexes, although we did not achieve C−H bond activation of the cationic rhodium complexes bearing the PN ligand. Despite using the same ligand system, the structure of the complexes was completely different because the metal center was changed from iridium to rhodium. To this end, we report unexpected different reactivities of the iridium(III) and rhodium(III) complexes in the ligand exchange reaction of phosphines, which are caused by different steric environments around the metal center due to the coordination pattern of the PCN ligand.

Results and Discussion

Synthesis of Neutral Iridium(III) Complexes Bearing the PN Ligand. When 0.5 equiv of $[IrCl(coe)]_2$ (coe = cyclooctene) was treated with 1 equiv of the PN ligand in the presence of PPh_3 (1 equiv) in toluene at 120 °C for 3 h, an intramolecular C−H bond activation occurred to give a neutral iridium(III) hydride complex, (PCN-κ^3*P*,*C*,*N*)Ir(H)(Cl)(PPh_3) (PCN = $Ph_2PC_6H_4CHOCH_2C_5H_4N$) (**1a**), in 80% isolated yield as a white solid (eq 1). The reaction proceeded even at room temperature for 12 h to afford **1a** in a similar yield. In the cationic iridium system, both iridium(I) and iridium(III) complexes could be isolated; however, we did not observe the iridium(I) species such as (PN-κ^2*P*, *N*)Ir(Cl)(coe) or (PN-κ^2*P*,*N*)-Ir(Cl)(PPh_3) at the initial stage of the reaction.[28]



The ^{1}H NMR spectrum of **1a** in C_6D_6 displayed a hydride signal with a doublet of doublet pattern (J = 11.3, 19.9 Hz) at −20.40 ppm, which is the typical chemical shift of a hydride ligand bound to iridium(III), indicating that the hydride atom is placed in a *cis* position to two phosphorus atoms.[32−34] The presence of the hydride ligand was also confirmed by the IR spectrum (2196 cm^{-1}). The PN ligand acts as a P−C−N tridentate ligand and coordinates to the iridium(III) center in a meridional manner. The one-proton signal with a doublet pattern (J = 6.7 Hz) at 6.23 ppm was assigned to the proton on the carbon directly bound to the iridium(III) center. When using a deuterium-labeled PN ligand (*o*-$Ph_2PC_6H_4CD_2OCH_2C_5H_4N$-2), both the hydride signal and the signal at 6.23 ppm disappeared completely in the ^{1}H NMR spectrum of the corresponding complex, indicating that the intramolecular C−H bond activation occurred at the benzylic position of the PN ligand. The ^{31}P NMR spectrum displayed two singlet signals (δ 6.16 and 13.24), whose integration, chemical shifts, and very weak coupling constants indicated that two kinds of phosphorus atoms, derived from the diphenylphosphino group in the PCN ligand, and PPh_3 coordinated to the iridium(III) center in a *cis* position.[35,36] Coordination of the pyridyl group in the PN ligand was confirmed by IR and ^{1}H NMR spectra. The C=N stretching vibration at 1606 cm^{-1}

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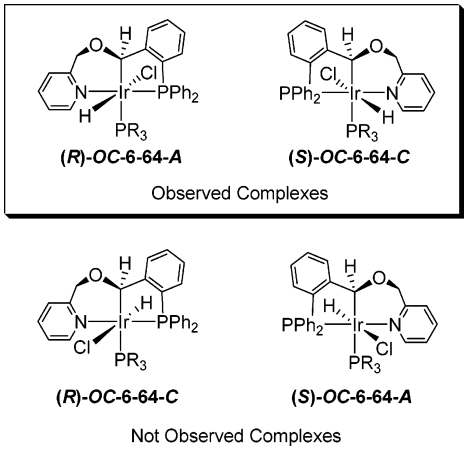


Figure 1. Isomers of the iridium complexes **1**.

was shifted to a higher wavenumber by ca. 10 cm^{-1} compared to that of the free PN ligand (1590 cm^{-1}), which is a characteristic shift for the coordination of the pyridine ring in the PN and PCN ligands to the metal center. The proton at the 6-position of the pyridine ring appeared at 8.31−8.41 ppm, which was not shifted from that of the free PN ligand (8.38−8.43 ppm), and had the characteristic shape of a *trans*-coordinated PN ligand, indicating meridional coordination of the PCN ligand. Two inequivalent methylene protons at the α-position of the 2-pyridyl group in the PCN ligand appeared at 4.75 and 5.18 ppm as a doublet pattern (J = 12.6 Hz), indicating that the PCN ligand formed a rigid bicyclo chelating ring by forming an Ir−C bond.

Complex **1a** has at least two diastereomers [(*S*)-*OC*-6-64-*C*/(*R*)-*OC*-6-64-*A* and (*R*)-*OC*-6-64-*C*/(*S*)-*OC*-6-64-*A*] arising from two stereogenic central chiralities due to a carbon center in the PCN ligand and the iridium center (Figure 1). The ^{1}H and ^{31}P NMR spectra of the reaction mixture before the purification revealed that complex **1a** formed as a single isomer. A nuclear Overhauser effect was not detected between the hydride proton at −20.40 ppm and the proton on the carbon directly bound to the iridium(III) center at 6.23 ppm. These spectral data suggested that complex **1a** was an (*S*)-*OC*-6-64-*C*/(*R*)-*OC*-6−64-*A* isomer in which the relative position of the two protons was *trans*, and this observation was consistent with the structure determined by the following X-ray analysis of **1a** (vide infra).

Recrystallization of **1a** from hexanes and THF gave colorless single crystals suitable for X-ray analysis. An ORTEP drawing is shown in Figure 2, selected bond distances and angles are given in Table 1, and relevant crystal and data parameters are presented in Table 3 (see Experimental Section). Although both (*S*)-*OC*-6-64-*C* and its enantiomer (*R*)-*OC*-6-64-*A* crystallized in the unit cell due to the centrosymmetric space group $P2_1/c$, the structure of only one isomer [(*S*)-*OC*-6-64-*C*] is shown in Figure 2. A notable structural feature is that the PCN ligand coordinates to the iridium(III) center by P(1), C(7), and N atoms in a meridional manner, in sharp contrast to the facial geometry of the PCN ligand in a cationic iridium(III) hydride complex [(PCN-κ^3*P*,*C*,*N*)Ir(H)(cod)]PF_6 (cod = cyclooctadiene).[28] The geometry around the iridium(III) center is distorted octahedral with one coordination site occupied by the hydride ligand, which

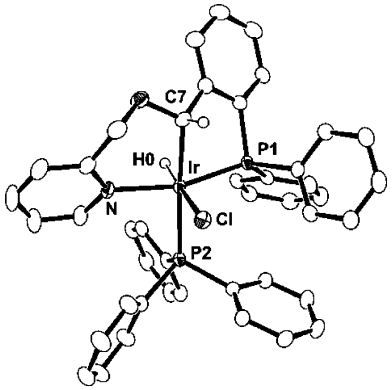


Figure 2. ORTEP drawing of complex **1a** with the atom-numbering scheme. The enantiomer, (*S*)-*OC*-6-64-*C*, is shown. The hydride ligand was not located in the actual structure determination.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 1a

Ir−P(1)	2.2559(7)	Ir−C(7)	2.139(3)
Ir−P(2)	2.3922(7)	Ir−Cl	2.4919(7)
Ir−N	2.162(2)		
C(7)−Ir−N	89.19(10)	P(1)−Ir−P(2)	99.77(2)
C(7)−Ir−P(1)	78.48(8)	C(7)−Ir−Cl	87.36(8)
N−Ir−P(1)	164.17(6)	N−Ir−Cl	90.54(6)
C(7)−Ir−P(2)	176.59(8)	P(1)−Ir−Cl	98.68(2)
N−Ir−P(2)	93.03(7)	P(2)−Ir−Cl	90.04(2)

was confirmed by the ^{1}H NMR and IR spectra. Two bulkier ligands, PPh_3 and the diphenylphosphino group in the PCN ligand, cause distortion around the iridium center. For example, the angle of C(7)−Ir−P(1) [78.48(8)°] was significantly smaller than 90° and P(1)−Ir−P(2) [99.77(2)°] was larger than 90°, although that of C(7)−Ir−N [89.19(10)°] was nearly a right angle. The angle of N−Ir−P(1) [164.17(6)°] was also markedly different from 180°.

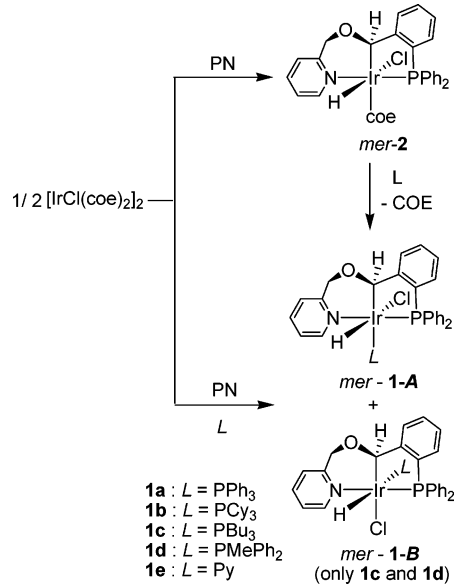
In our previous studies of cationic complexes bearing the PCN/CH_3 ligand, the facial isomer of the iridium(III) hydride complex was gradually converted to the meridional isomer.[29] In the ^{1}H NMR analysis of the reaction for the preparation of **1a** from $[IrCl(coe)_2]_2$, the PN ligand, and PPh_3, we could not confirm the presence of the facial isomer. There was no reaction when a solution of **1a** was heated in toluene at 150 °C, and complex **1a** was recovered without decomposition.

Reaction of the PN ligand with $[IrCl(coe)]_2$ in the absence of PPh_3 at room temperature in toluene afforded a similar neutral iridium(III) complex, (PCN-κ^3*P*,*C*,*N*)Ir(H)(Cl)(coe) (**2**), quantitatively as an orange powder (Scheme 1). Complete purification of **2** was not successful due to its instability and high solubility in solvents. Complex **2**, however, was characterized by the usual spectroscopic and physical data. The chemical shift and a characteristic coupling pattern for the proton at the 6-position of the pyridine ring indicated that the PCN ligand was coordinated to the iridium(III) center in a meridional manner. The ^{1}H and ^{31}P NMR spectra of the reaction mixture before purification revealed that complex **2** was obtained as a single isomer. Although the relative configuration of **2** could not be determined from the spectral data, we estimated that complex **2** also formed as an (*S*)-*OC*-6-64-*C*/(*R*)-*OC*-6−64-*A* isomer from the structure of the phosphine complex obtained by the following ligand exchange reaction. Complex **2** reacted with PPh_3 in C_6D_6 at room temperature within 1 h to afford **1a** as a single (*S*)-*OC*-6-64-*C*/(*R*)-*OC*-6-64-*A* isomer quantitatively along with 1 equiv of free cyclooctene.

Reactions of the PN ligand with $[IrCl(coe)_2]_2$ in the presence of other phosphines such as PCy_3, PBu_3, and $PMePh_2$ or pyridine

(36) For recent examples of iridium phosphine complexes showing very weak couplings, see: (a) Janka, M.; Atesin, A. C.; Fox, D. J.; Flaschenriem, C.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2006**, *45*, 6559. (b) Janka, M.; He, W.; Frontier, A. J.; Flaschenriemand, C.; Eisenberg, R. *Tetrahedron* **2005**, *61*, 6193. (c) Janka, M.; He, W.; Frontier, A. J.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 6864. (d) Albietz, P. J., Jr.; Cleary, B. P.; Paw, W.; Eisenberg, R. *J. Am. Chem. Soc.* **2001**, *123*, 12091.

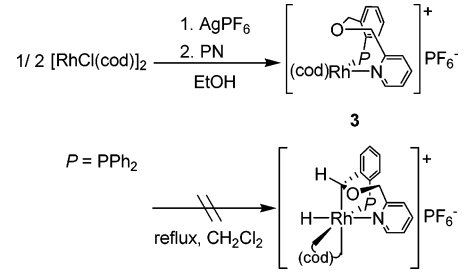
Scheme 1



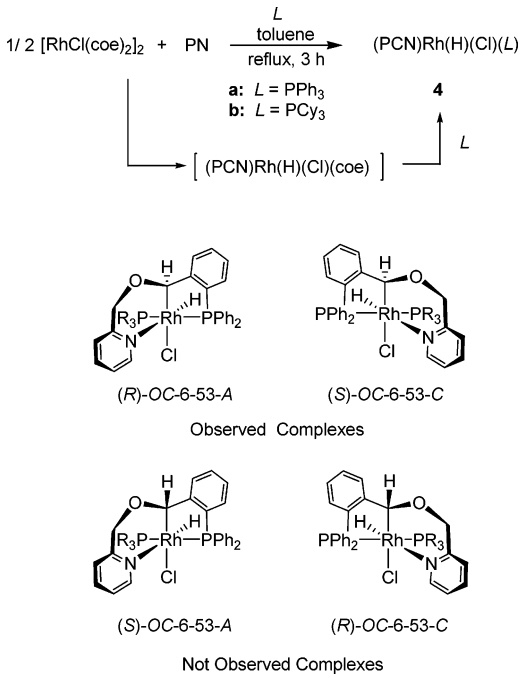
(=Py) afforded a series of neutral iridium(III) hydride complexes, (PCN-κ^3*P,C,N*)Ir(H)(Cl)(*L*) [*L* = PCy_3 (**1b**), PBu_3 (**1c**), $PMePh_2$ (**1d**), Py (**1e**)]. The reactions of the phosphines proceeded at room temperature, while the reaction of the pyridine required reflux conditions. All the complexes were isolated in good yield, and the PCN ligand coordinated to the iridium(III) center in a meridional manner (Scheme 1). The ^{31}P NMR and ^{1}H NMR spectra of PCy_3 complex **1b** and pyridine complex **1e** indicated the formation of only one isomer, which had a structure similar to that of the PPh_3 complex **1a** and the coe complex **2**, while those of other phosphine complexes **1c** and **1d** exhibited a mixture of two isomers. For example, the phosphorus signals of **1d**-minor in the ^{31}P NMR spectrum appeared at −14.46 (singlet) and 15.97 ppm (singlet) and that of **1d**-major at −15.96 (singlet) and 15.27 ppm (singlet). The hydride signal of **1d**-minor in the ^{1}H NMR spectrum appeared at −20.73 ppm with a doublet of doublets pattern (J = 11.8, 20.2 Hz) and that of **1d**-major at −10.00 ppm with a doublet of doublets pattern (J = 19.8, 160.6 Hz). The coupling constants of **1d**-minor were similar to those of the PPh_3 complex **1a** and the PCy_3 complex **1b**, and that of **1d**-major was clearly different. The complexes **1c**-major and **1c**-minor also had similar coupling constants. As shown in Scheme 1, we determined that the structure of the minor isomer of **1c** and **1d** was ***A***, which is similar to the structure of **1a** and **1b**, and the structure of major isomers was ***B***, in which one of the two phosphorus atoms was placed in the *cis* position to the hydride ligand and another was in the *trans* position.[33]

Synthesis of Neutral Rhodium(III) Complexes Bearing the PN Ligand. The cationic rhodium(I) complex bearing the PN ligand, [(PN-κ^2*P,N*)Rh(cod)]PF_6 (**3**), could be prepared using a method similar to that for the synthesis of the iridium(I) analogue [(PN-κ^2*P,N*)Ir(cod)]PF_6.[28] Reaction of $[RhCl(cod)]_2$ with 2 equiv of the PN ligand in the presence of excess $AgPF_6$ in ethanol at room temperature for 5 h gave **3** as an orange powder in 87% yield (Scheme 2). The structure of **3** was fully characterized by spectral and physical data including elemental analysis. The ^{1}H NMR of **3** in $CDCl_3$ at 30 °C showed broad signals, especially for the protons at two kinds of methylene protons in the PN ligand. As the temperature decreased, the signals sharpened to provide four inequivalent doublet peaks at 4.73 (J = 13.1 Hz), 4.81 (J = 15.6 Hz), 5.13 (J = 13.1 Hz), and 5.30 (J = 15.6 Hz) ppm at −20 °C, indicating that the

Scheme 2



Scheme 3



chelate chain of the PN ligand showed rapid dynamic behavior, including coordination and dissociation of the oxygen atom. In contrast to [(PN-κ^2*P,N*)Ir(cod)]PF_6, intramolecular C−H bond activation of **3** did not proceed at all in $CDCl_3$ at 30 °C or even in 1,2-dichloroethane at 80 °C, and complex **3** was recovered without decomposition. When $[RhCl(coe)_2]_2$ was used as a starting rhodium(I) complex instead of $[RhCl(cod)]_2$, the reaction afforded a complex mixture and neither the rhodium(I) complexes [(PN-κ^2*P,N*)Rh(coe)]PF_6 nor the rhodium(III) hydride complex [(PCN-κ^3*P,C,N*)Rh(H)$(coe)_2$]PF_6 was observed.

In a neutral rhodium system, intramolecular C−H bond activation proceeded similarly to the neutral iridium system to afford the corresponding rhodium(III) hydride complex. Treatment of $[RhCl(coe)_2]_2$ with the PN ligand in the presence of PR_3 (R = Ph, Cy) in toluene afforded the neutral rhodium(III) hydride complexes (PCN-κ^3*P,C,N*)Rh(H)(Cl)(PR_3) [R = Ph (**4a**), Cy (**4b**)] as pale yellow powders in modest isolated yields (Scheme 3). Similar to the iridium complex **1a**, the ^{1}H and ^{31}P NMR analysis of the reaction mixture demonstrated that complexes **4a** and **4b** were also composed of a single diastereomer.

The structure of **4a**, which was determined by the usual spectroscopic and physical data as well as X-ray analysis, was clearly different from that of the iridium analogue complex **1a**. Recrystallization of **4a** from hexanes and THF gave single orange crystals suitable for X-ray analysis. The ORTEP drawing of **4a** is shown in Figure 3, selected bonds and angles are listed in Table 2, and relevant crystal and data parameters are presented

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 4a

Rh−P(1)	2.302(3)	Rh−C(7)	2.068(7)
Rh−P(2)	2.279(3)	Rh−Cl	2.5207(12)
Rh−N	2.201(4)		
C(7)−Rh−N	91.7(2)	P(2)−Rh−P(1)	169.30(5)
C(7)−Rh−P(1)	94.4(2)	C(7)−Rh−Cl	172.8(2)
N−Rh−P(1)	94.7(3)	N−Rh−Cl	91.13(12)
C(7)−Rh−P(2)	82.2(2)	P(2)−Rh−Cl	90.94(11)
N−Rh−P(2)	95.5(3)	P(1)−Rh−Cl	91.93(11)

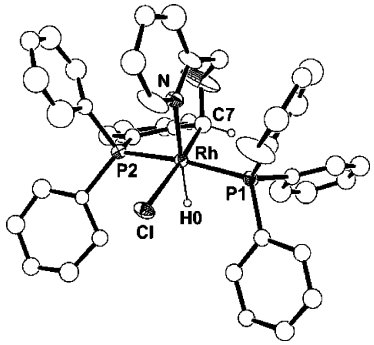


Figure 3. ORTEP drawing of complex **4a** with the atom-numbering scheme. The enantiomer, (*S*)-*OC*-6-53-*C*, is shown. The hydride ligand was not located in the actual structure determination.

in Table 3 (see Experimental Section). The centrosymmetric space group $P2_1$ indicated that the crystals of **4a** also included a pair of enantiomers, (*S*)-*OC*-6-53-*C* and (*R*)-*OC*-6-53-*A*, and Figure 2 shows only the structure of the (*S*)-*OC*-6-53-*C* isoform. The structure has an octahedral geometry around the rhodium(III) center. The PN ligand acted as a P−C−N tridentate ligand and coordinated to the rhodium(III) center in a facial manner. Each phosphine atom bound to the rhodium atom was located at a *trans* position. A similar metal coordination system is observed in cationic iridium complexes bearing PCN or PCN/CH_3 ligands.[28,29]

When the rhodium complex $[RhCl(coe)_2]_2$ was treated with the PN ligand in the presence of PPh_3 in toluene at room temperature, the reaction mixture immediately turned to a red solution and then slowly changed to a yellow solution. Five minutes after starting the reaction, before the color of the reaction mixture turned yellow, the addition of hexanes to the reaction mixture afforded an orange precipitation. ^{1}H NMR analysis of the orange solid in C_6D_6 indicated the formation of two complexes bearing the PN and/or PCN ligand. Two signals of the proton at the 6-position of the pyridine ring appeared at 9.24 and 10.28 ppm (Figure 4a), neither of which are the signal of **4a** (9.58 ppm). A coupling pattern of the signal at 9.24 ppm showed a characteristic shape for the *cis* or facial coordination of the PN or PCN ligand, and that at 10.28 ppm indicated the *trans* or meridional coordination. In the hydride signal region, only one signal was observed at −19.04 ppm with a doublet of doublets pattern (J = 19.2, 31.0 Hz), indicating that one of the two signals described above was derived from a rhodium(I) complex with no hydride ligand.[37]

In the ^{1}H NMR of a C_6D_6 solution of the orange solid after 18 h at room temperature, the signal of **4a** appeared along with the signals described above (Figure 4b). Heating a toluene solution of the orange solid under reflux conditions for 3 h

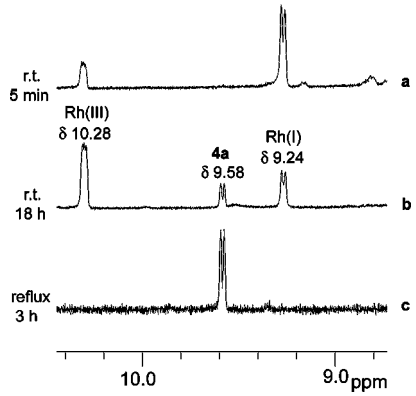


Figure 4. H6 of the pyridine ring monitored by ^{1}HNMR spectroscopy.

afforded a yellow solution, in which the ^{1}H NMR displayed that all the red solids were converted to **4a** (Figure 4c). The hydride signal in the ^{1}H NMR spectrum also transformed to the signals for **4a**. Although the red solids could not be isolated as a pure solid and the structure of two rhodium species observed in the ^{1}H NMR spectrum of Figure 4a was not determined completely, we assumed the formation of a rhodium(I) complex such as *cis*-(PN-κ^2*P*,*N*)RhCl(coe) and the rhodium(III) hydride complex bearing the PCN ligand in a meridional manner. In the reaction for the preparation of **4** from $[RhCl(coe)_2]_2$, the rhodium(I) complexes formed and then the intramolecular C−H bond activation afforded the meridional rhodium(III) hydride complex, followed by isomerization to give thermodynamically stable complex **4a** or **4c**.

Ligand Exchange Reaction. The coordination ability of various tertiary phosphines (PR_3) to the metal center can be controlled by changing the substituent (R) of the phosphines electronically and sterically. C. A. Tolman quantified the steric and electronic factors of the phosphine ligand.[38] The reactivities of most organometallic compounds in the ligand exchange reaction of phosphines, however, are explained by the combination of both factors, and it is very difficult to make proper use of both factors in a similar ligand system. Using the phosphine ligand exchange reaction as one of the most primitive metal-meditated reactions, we demonstrated an unexpected difference in the reactivity of iridium(III) and rhodium(III) hydride complexes and showed that the coordination geometry of the PCN ligand to the metal center is the predominant factor for controlling the reactivity of the complexes using Tolman's parameter.

We examined the ligand exchange reaction of these iridium(III) and rhodium(III) complexes with various tertiary phosphines. When the iridium PPh_3 complex **1a** bearing the meridional-coordinated PCN ligand was treated with 1 equiv of PCy_3 in toluene at room temperature for 24 h, the phosphine ligand exchange reaction proceeded to some extent to afford the PCy_3 complex **1b** in 20% yield along with the recovered **1a** in 80% yield and free PPh_3 and PCy_3 (eq 2), whereas complex **1b** reacted with 1 equiv of PPh_3 smoothly under similar conditions to afford **1a** quantitatively (eq 3). According to Tolman's parameter, the steric factor of PPh_3 (145°) was smaller than that of PCy_3 (170°), which indicates that the coordination of PPh_3 was favorable under the steric controls. In addition, the electronic factor of PCy_3 [ν(CO) 2056.4 cm^{-1}] was larger than that for PPh_3 [ν(CO) 2068.9 cm^{-1}], which indicates that the coordination of PCy_3 was favorable under the electronic controls (Figure 5).

(37) The ^{31}P NMR spectrum for the orange solids in C_6D_6 indicated the presence of more than two species except **4a**: one species at 47.8 ppm (broad multiplet), second species at 51.35 (dd, J = 44.8, 194.5 Hz) and 53.29 (dd, J = 44.8, 194.5 Hz), and another species at 58.58 (d, J = 163.4 Hz).

(38) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

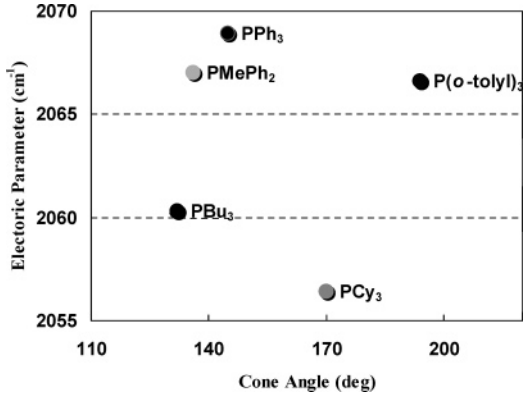
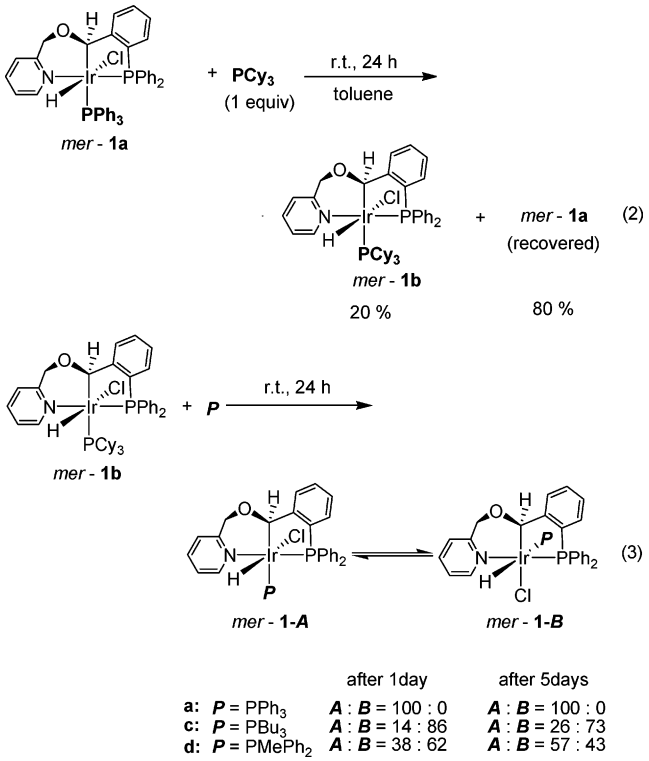


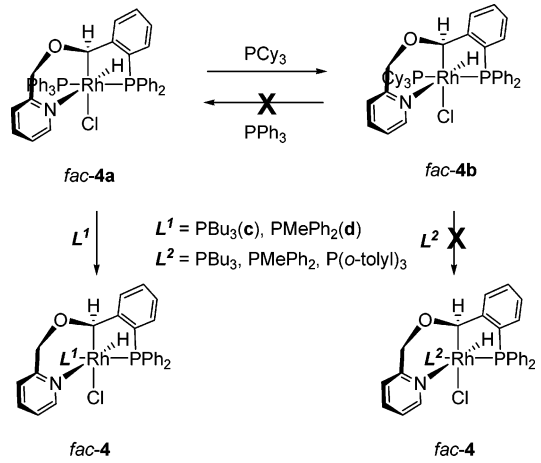
Figure 5. Cone angle and electronic parameter of various tertiary phosphine ligands.

The results shown in eqs 2 and 3 suggest that the ligand exchange reaction of phosphines in the iridium(III) complexes bearing the meridional-coordinated PCN ligand was controlled primarily by the steric effect of the coming phosphine ligand. Similar reactivity was observed in the reaction with other phosphines. Under conditions similar to those described above, the PCy_3 complex **1b** reacted easily with PBu_3 or $PMePh_2$, which had smaller cone angles than that of PCy_3, to afford the corresponding phosphine complex **1c** or **1d**, but did not react with P(*o*-tolyl)$_3$, which has a larger cone angle.

Interestingly, phosphine complexes **1c** and **1d** were obtained as a mixture of two isomers, **1c-*A*** and **1c-*B*** and **1d-*A*** and **1d-*B***, which were the same two isomers observed in the reaction of $[IrCl(coe)_2]_2$ with the PN ligand (vide supra). The ^{1}H and ^{31}P NMR spectra of the ligand exchange reaction after 1 day showed that the ratios of ***A*** and ***B*** isomers were 14:86 for **1c** and 38:62 for **1d**. Isomerization from ***A*** to ***B*** occurred gradually in C_6D_6 at room temperature, and the ratios of the ***A*** isomer after 5 days increased to 26% and 57%, respectively, indicating that the ***A*** isomer was a thermodynamic product and the ***B*** isomer was a kinetic product. Selectivity of ***A*** and ***B*** isomers



Scheme 4



was controlled by a combination of the steric factor and the *trans* influence. A higher *trans* influence of the hydride ligand compared to the carbon in the PCN ligand facilitates the isomerization of the ***A*** isomer to the ***B*** isomer.[39] The steric effect of the phosphine ligand was superior to the *trans* influence: when using bulkier phosphines such as PPh_3, the ***B*** isomer was not observed at all, but for **1c** and **1d**, which have smaller phosphines such as PBu_3 or $PMePh_2$, the decreased steric repulsion allowed for the formation of the ***B*** isomer as a kinetic product. The meridional coordination geometry of the PCN ligand creates an environment around the iridium center that is sensitive to the steric nature.

In contrast to the phosphine ligand exchange reaction of the iridium complexes, the corresponding rhodium complexes bearing the facial-coordinated PCN ligand had different reactivities. For example, the rhodium PPh_3 complex **4a** reacted easily with PCy_3, which had a larger cone angle than PPh_3, in toluene at room temperature for 12 h to afford the PCy_3 complex **4b** with 80% conversion, while the ligand exchange reaction did not proceed at all between the iridium PCy_3 complex **4b** and PPh_3 (Scheme 4). These observations suggest that the ligand exchange reaction in the rhodium complexes bearing the facial-coordinated PCN ligand was controlled not by the bulkiness of the phosphine ligand (steric factor) but rather by the basicity of the phosphine ligand (electronic factor).

To confirm our findings, we examined the ligand exchange reaction with other phosphines. Although PCy_3 of **4b** could not be substituted for PBu_3, $PMePh_2$, and P(*o*-tolyl)$_3$, which had smaller electronic parameters, the rhodium PPh_3 complex **4a** reacted with PBu_3 and $PMePh_2$ in toluene at room temperature to afford the corresponding phosphine complexes. Through all ligand exchange reactions, the obtained rhodium complexes were a single isomer, (*S*)-*OC*-6-53-*C* and (*R*)-*OC*-6-53-*A*. Other isomers, including (*R*)-*OC*-6-53-*C* and (*S*)-*OC*-6-53-*A*, were not observed in the ^{1}H and ^{31}P NMR analysis. The stability of the rhodium complexes with the facial-coordinated PCN ligand was controlled only by the electronic factor of the phosphines: the environment around the rhodium center constructed by the PCN ligand with a facial coordination geometry was not very sensitive to the steric nature that the coordination ability to the metal center depended on the basicity of the incoming phosphines. Although the iridium(III) and rhodium(III) hydride complexes bearing the same PCN ligand system are different only with regard to the coordination pattern of the ligand, the controlling factor for the proceeding ligand exchange reaction is dramatically changed.

Experimental Section

All reactions and manipulations were performed under argon by use of standard vacuum line and Schlenk tube techniques. ^{1}H NMR spectra were recorded at either 300 MHz on a Varian Mercury 300 spectrometer or at 270 MHz on a JEOL JNM-GSX270 spectrometer. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane or referenced to the chemical shifts of residual solvent resonances (C_6H_6 or CH_3Cl was used as internal standard, δ 7.20 or 7.26). ^{31}P{^{1}H} NMR spectra were recorded at 121.49 MHz on a Varian Mercury 300 spectrometer or at 109.25 MHz on a JEOL JNM-GSX270 spectrometer, and chemical shifts were referenced to external 85% H_3PO_4. Infrared spectra were recorded on a JASCO FT/IR-230 instrument. Mass spectra were obtained on a JEOL JMS DX-303HF spectrometer. Elemental analyses were recorded on a Perkin-Elmer 2400 instrument at the Faculty of Engineering Science, Osaka University. All melting points were recorded on a Yanaco MP-52982 instrument and were not corrected.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Dichloromethane was distilled from calcium hydride under argon prior to use. Tetrahydrofuran, toluene, and hexanes were distilled over sodium benzophenone ketyl under argon prior to use, and other solvents for recrystallization were dried using standard procedures. The starting materials, $[IrCl(coe)_2]_2$, $[RhCl(coe)_2]_2$, $[RhCl(cod)]_2$, and the PN ligand, *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2, were prepared according to published procedures.[25,26,40,41] PPh_3 and PCy_3 were recrystallized from ethanol prior to use.

Preparation of *mer*-(PCN-κ^3*P,C,N*)Ir(H)(Cl)(PPh_3) (1a). A stirred mixture of $[IrCl(coe)_2]_2$ (317 mg, 0.350 mmol), the PN ligand (290 mg, 0.760 mmol), and PPh_3 (203 mg, 0.780 mmol) in toluene (5 mL) was heated to 120 °C for 3 h. The mixture was cooled to ambient temperature for a period of 30 min. After the solvent was removed in vacuo, the residue was dissolved in THF (1 mL), and then hexanes (5 mL) were added. A white precipitate was collected by removal of the solvent with syringe and washed with hexanes (5 mL). The residue was dried in vacuo to give **1a** as white solids (530 mg, 80% yield). Mp: 187 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ −20.40 (dd, J_{H-P} = 11.3, 19.9 Hz, 1H, Ir-*H*), 4.75 (d, J_{H-H} = 12.6 Hz, 1H, O-C*H*$_2$-Py), 5.18 (d, J_{H-H} = 12.6 Hz, 1H, O-C*H*$_2$-Py), 5.40−5.47 (m, 1H, H4 of Py), 6.23 (d, J_{H-H} = 6.7 Hz, 1H, Ar-C*H*-O), 6.26−7.43 (m, 30H, H of arom), 7.79−7.89 (m, 1H, H5 of Py), 8.31−8.41(m, 1H, H6 of Py). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 6.16 (s), 13.24 (s). FABMS: *m*/*z* = 836 (M^+ − Cl). IR (KBr tablet, cm^{-1}): ν 2196, 1606, 1095. Anal. Calcd for $C_{43}H_{37}IrClNOP_2$: C, 59.13; H, 4.27; N, 1.60. Found: C, 58.48; H, 4.20; N, 1.56.

Preparation of *mer*-(PCN-κ^3*P,C,N*)Ir(H)(Cl)(PCy_3) (1b). A mixture of $[IrCl(coe)_2]_2$ (99 mg, 0.110 mmol), the PN ligand (84 mg, 0.220 mmol), and PCy_3 (63 mg, 0.220 mmol) in toluene (5 mL) was stirred at room temperature for 3 h. After the solvent was removed in vacuo, the residue was dissolved in THF (1 mL) and then hexanes (5 mL) were added. A white precipitate was collected by removal of the solvent with syringe and washed with hexanes (5 mL). The residue was dried in vacuo to give **1b** as a white solid (163 mg, 83% yield). Mp: 189 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ −20.38 (t, J_{H-P} = 16.1 Hz, 1H, Ir-*H*), 0.40−2.40 (m, 33H, H of PCy_3), 4.79 (d, J_{H-H} = 11.8 Hz, 1H, O-C*H*$_2$-Py), 5.62 (d, J_{H-H} = 11.8 Hz, 1H, O-C*H*$_2$-Py), 6.41 (d, J = 2.5 Hz, 1H, Ar-C*H*-O), 6.50−7.25 (m, 18H, H of arom), 9.83−9.88 (m, 1H, H6 of Py). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 1.46 (s), 22.32 (s). FABMS: *m*/*z* = 856 (M^+ − Cl), 610 (M^+ − PCy_3), 573 (M^+ − Cl − PCy_3). IR (KBr tablet, cm^{-1}): ν 2239, 1605, 1043. Anal. Calcd for $C_{43}H_{55}IrClNOP_2$: C, 57.93; H, 6.22; N, 1.57. Found: C, 57.54; H, 6.11; N, 1.56.

Table 3. Crystal and Refinement Data for 1a and 4a

	1a	4a
color	colorless	colorless
empirical formula	$C_{43}H_{37}P_2NOIr$	$C_{43}H_{37}ClRhNOP_2$
fw	873.33	784.04
radiation/Å	Mo Kα (monochr) 0.71075	Mo Kα (monochr) 0.71075
T/K	120	120
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$
unit cell dimens		
a/Å	16.5795(8)	9.2620(5)
b/Å	10.2514(4)	23.8082(13)
c/Å	22.4112(9)	9.1824(4)
β/deg	109.4691(16)	117.471(2)
V/Å^3	3591.3(2)	1796.51(15)
Z	4	2
d_{calc}/g cm^{-3}	1.615	1.449
μ/mm^{-1} (Mo Kα)	3.917	0.674
cryst size/mm	0.27 × 0.20 × 0.12	0.37 × 0.20 × 0.10
no. of total, unique reflns	12 7780, 10 473	64 480, 10 811
R_{int}	0.0738	0.0659
transmn range	0.4845−0.7111	0.5705−0.9349
no. of params, restraints	590, 0	241, 27
R,[a] R_w,[b] GOF	0.0289, 0.0667, 1.110	0.0744, 0.2054, 1.078
resid density/e Å^{-3}	−1.69 < 1.787	−1.059 < 3.164

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$, for all $I > 2.0\sigma(I)$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$.

Preparation of (PCN-κ^3*P,C,N*)Ir(H)(Cl)(PBu_3) (1c). Method A: A toluene (1 mL) solution of PBu_3 (11 mg, 0.053 mmol) was added dropwise to a stirred toluene (1 mL) solution of $[IrCl(coe)_2]_2$ (24 mg, 0.027 mmol) and the PN (21 mg, 0.053 mmol). The solution was stirred at room temperature for 12 h. Solvent was removed in vacuo to give **1c** as an orange powder (quantitative yield) as a mixture of **1c-*A*** and **1c-*B*** (**1c-*A*:1c-*B*** = 11:89; the ratio was determined by ^{1}H and ^{31}P NMR). **Method B:** A toluene (1.5 mL) solution of PBu_3 (3 mg, 0.016 mmol) was added dropwise to a stirred toluene (1 mL) solution of **1a** (14 mg, 0.016 mmol). The solution was stirred at room temperature for 24 h. Solvent was removed in vacuo to give **1c** as an orange powder (14 mg, quantitative yield) as a mixture of **1c-*A*** and **1c-*B*** (**1c-*A*:1c-*B*** = 14:86; the ratio was determined by ^{1}H and ^{31}P NMR). IR (NaCl nujol, cm^{-1}): ν 2362, 1582,1090. ^{1}H NMR (300 MHz, C_6D_6): **1c-*A***, δ −20.69 (dd, J_{P-H} = 12.7 18.8 Hz, 1H, Ir-*H*), 0.18−1.85 (m, PBu_3), 4.74 (d, J_{H-H} = 12.4 Hz, 1H, −O-C*H*$_2$-py), 5.36 (d, J_{H-H} = 12.4 Hz, 1H, −O-C*H*$_2$-py), 6.38−8.55 (m, arom), 9.68−9.76 (m, 1H, H6 of py); **1c-*B***, δ −10.04 (dd, J_{P-H} = 20.0 150.4 Hz, 1H, Ir-*H*), 0.18−1.85 (m, P*Bu*$_3$), 4.43 (d, J_{H-H} = 13.6 Hz, 1H, −O-C*H*$_2$-py), 4.84 (d, J_{H-H} = 13.6 Hz, 1H, −O-C*H*$_2$-py), 6.38−8.55 (m, arom), 10.30−10.38 (m, 1H, H6 of py). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): **1c-*A***, −21.11 (s), 23.20 (s); **1c-*B*,** δ −18.60 (s), 15.79 (s). FABMS: *m*/*z* = 778 (M^+ − Cl), 573 (M^+ − PBu_3− Cl). Complete purification of **1e** for satisfaction of elemental analysis was not successful due to high solubility to solvents and its instability.

Preparation of (PCN-κ^3*P,C,N*)Ir(H)(Cl)($PMePh_2$) (1d). Method A: A toluene (1 mL) solution of $PMePh_2$ (33 mg, 0.164 mmol) was added dropwise to a stirred toluene (1 mL) solution of $[IrCl(coe)_2]_2$ (73 mg, 0.082 mmol) and the PN (63 mg, 0.164 mmol). The solution was stirred at room temperature for 12 h. Solvent was removed in vacuo to give **1d** as an orange powder (quantitative yield) as a mixture of **1d-*A*** and **1d-*B*** (**1d-*A*:1d-*B*** = 30:70; the ratio was determined by ^{1}H and ^{31}P NMR). **Method B:** A toluene (1.5 mL) solution of $PMePh_2$ (13 mg, 0.064 mmol) was added dropwise to a stirred toluene (1 mL) solution of **1a** (56 mg, 0.064 mmol). The solution was stirred at room temperature for 24 h.

(39) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Cood. Chem. Rev.* **1973**, *10*, 335.
(40) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 90.
(41) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 91.

Solvent was removed in vacuo to give **1d** as an orange powder (68 mg) as a mixture of **1d-*A*** and **1d-*B*** (**1d-*A*:1d-*B*** = 38:62; the ratio was determined by ^{1}H and ^{31}P NMR). IR (NaCl nujol, cm^{-1}): ν 2190, 2054, 1606,1095. ^{1}H NMR (300 MHz, C_6D_6): **1d-*A***, δ −20.73 (dd, J_{P-H} = 11.8, 20.2 Hz, 1H, Ir-*H*), 1.65 (d, J_{P-H} = 7.4 Hz, 3H, PC*H*$_3$Ph$_2$), 4.32 (d, J_{H-H} = 13.7 Hz, 1H, −O-C*H*$_2$-py), 4.80 (d, J_{H-H} = 13.7 Hz, 1H, −O-C*H*$_2$-py), 6.04 (t, J_{H-H} = 6.6, 1H, H4 of py), 6.26 (d, J = 7.5 Hz, 1H, Ar-C*H*-O), 5.82−8.52 (m, arom), 9.58−9.62 (m, 1H, H6 of py); **1d-*B***, δ −10.00 (dd, J_{P-H} = 19.8, 160.6 Hz, 1H, Ir-*H*), 1.94 (d, J_{P-H} = 7.4 Hz, 3H, PC*H*$_3$Ph$_2$), 5.07 (d, J_{H-H} = 12.6 Hz, 1H, −O-C*H*$_2$-py), 5.16 (d, J_{H-H} = 12.6 Hz, 1H, −O-C*H*$_2$-py), 5.85 (t, J_{H-H} = 6.4, 1H, H4 of py), 6.51 (d, J = 8.4 Hz, 1H, Ar-C*H*-O), 5.82−8.52 (m, arom), 8.66−8.73 (m, 1H, H6 of py). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): **1d-*A***, δ −14.46 (s), 15.97 (s); **1d-*B***, δ −15.96 (s), 15.27 (s). FABMS: m/z = 776 (M^+ − Cl), 573 (M^+ − PMePh$_2$− Cl). Complete purification of **1e** for satisfaction of elemental analysis was not successful due to high solubility to solvents and its instability.

Preparation of (PCN-κ^3*P,C,N*)Ir(H)(Cl)(Py) (1e). A toluene (1 mL) solution of pyridine (0.05 mL, excess) was added dropwise to a stirred toluene (1 mL) solution of [IrCl(coe)$_2$]$_2$ (74 mg, 0.083 mmol) and the PN (63 mg, 0.164 mmol). The solution was stirred at 120 °C for 3 h. After the solvent was removed in vacuo, the residue was washed with hexanes (5 mL). The residue was dried in vacuo to give **1e** as a white powder (91 mg, 60% yield) as a single isomer. Mp: 187 °C (dec). IR (KBr nujol, cm^{-1}): ν 2196, 1606, 1095. ^{1}H NMR (300 MHz, C_6D_6): δ −20.86 (d, J_{H-P} = 23.4 Hz, 1H, Ir-*H*), 4.49 (d, J_{H-H} = 13.2 Hz, 1H, −O-C*H*$_2$-py), 5.08 (d, J_{H-H} = 13.2 Hz, 1H, −O-C*H*$_2$-py), 6.11−7.47 (m, arom) 8.19−8.31 (m, 1H, H6 of py), 9.68−9.80 (m, 1H, H6 of py of PN). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 20.61 (s). FABMS: m/z = 728 (M^+ + Cl), 655 (M^+ − Cl), 573 (M^+ − Cl − py). Anal. Calcd for $C_{30}H_{27}IrClN_2OP$: C, 52.21; H, 3.94; N, 4.06. Found: C, 52.20; H, 3.98; N, 4.12.

Preparation of (PCN-κ^3*P,C,N*)Ir(H)(Cl)(coe) (2). A mixture of [IrCl(coe)$_2$]$_2$ (22 mg, 0.025 mmol) and the PN ligand (18 mg, 0.047 mmol) in toluene (4 mL) was stirred at room temperature for 1 h. The solvent was removed in vacuo to give **2** as an orange powder (36 mg, quantitative yield). Mp: 134 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ −24.54 (d, J_{H-P} = 20.6 Hz, 1H, Ir-*H*), 1.01−2.72 (m, H of COE), 4.56 (d, J_{H-H} = 13.7 Hz, 1H, O-C*H*$_2$-Py), 4.76 (d, J_{H-H} = 13.7 Hz, 1H, O-C*H*$_2$-Py), 6.45 (d, J_{H-H} = 6.9 Hz, 1H, Ar-C*H*-O), 6.80−8.25 (m, H of Ar), 10.49−10.52 (m, 1H, H6 of Py). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 19.89 (s). FABMS: m/z = 573 (M^+ − Cl − PCy$_3$). IR (KBr tablet, cm^{-1}): ν 2360, 1606 cm^{-1}. Complete purification of **2** for satisfaction of elemental analysis was not successful due to high solubility to solvents and its instability.

Preparation of [(PN-κ^3*P,N*)Rh(cod)]PF$_6$ (3). An EtOH (2 mL) solution (2 mL) of AgPF$_6$ (120 mg, 0.475 mmol) was added dropwise to a stirred EtOH (5 mL) suspension of [RhCl(cod)]$_2$ (72 mg, 0.146 mmol) at room temperature. The reaction mixture was stirred at room temperature for 90 min. After removal of insoluble materials by filtration, the filtrate was added to an EtOH (2 mL) solution of the PN ligand (119 mg, 0.310 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 h. After the solvent was removed with a syringe, the obtained yellow solid was washed with EtOH (3 mL × 2) to give **3** (187 mg, 0.253 mmol) as an orenge powder. Recrystallization of the crude product from dichloromethane and ether gave a pure orange crystal. Mp: 207.5 °C (dec). ^{1}H NMR ($CDCl_3$, −20 °C, 270.05 MHz): δ 1.90−2.25 (m, 4H, methylene of COD), 2.45−2.72 (m, 4H, methylene of COD), 4.25−4.46 (br, 4H, olefin of COD), 4.73 (d, J = 13.1 Hz, 1H, O-C*H*$_2$-py), 4.81 (d, J = 15.6 Hz, 1H, Ar-C*H*$_2$-O), 5.13 (d, J = 13.1 Hz, 1H, O-C*H*$_2$-py), 5.30 (d, J = 15.6 Hz, Ar-C*H*$_2$-O), 6.30−6.43 (m, 1H, arom), 6.86−7.03 (m, 5H, arom), 7.20−7.38 (m, 4H, arom), 7.38−7.52 (m, 2H, arom), 7.58−7.72 (m, 3H, arom), 7.96−8.17 (m, 2H, arom), 8.84 (d, J = 5.4, 1H, H6 of py). ^{31}P{^{1}H} NMR (30 °C, $CDCl_3$): δ 15.8 (d, J = 141 Hz). FABMS: m/z = 594 (M^+ − PF$_6$). IR (nujol, cm^{-1}): ν 1604, 1083, 840, 753, 702. Anal. Found: C, 49.27; H, 4.27; N, 1.90. Calcd for $C_{33}H_{34}F_6RhNOP_2$: C, 49.54; H, 4.40; N, 1.94.

Preparation of *fac*-(PCN-κ^3*P,C,N*)Rh(H)(Cl)(PPh$_3$) (4a). Solid PPh$_3$ (31 mg, 0.120 mmol) was added to a stirred toluene (1 mL) suspension of [RhCl(coe)$_2$]$_2$ (46 mg, 0.060 mmol) and the PN ligand (43 mg, 0.120 mmol). The solution was stirred at 120 °C for 3 h. After the solvent was removed in vacuo, the residue was dissolved in THF (1 mL) and then hexanes (5 mL) were added. A white precipitate was collected by removal of the solvent with syringe and washed with hexanes (10 mL). The residue was dried in vacuo to give **4a** as a white powder (87 mg, 92% yield) as a single isomer. Mp: 158 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ −15.52 (ddd, J = 11.5, 11.5, 18.9 Hz, 1H, H of Ir-H), 3.76 (d, J_{H-H} = 15.4 Hz, 1H, H of O-C*H*$_2$-Py), 3.86 (d, J_{H-H} = 15.4 Hz, 1H, H of O-C*H*$_2$-Py), 5.73 (d, J = 7.4 Hz, 1H), 5.98−8.35 (m, H of Ar), 9.58 (d, , J = 4.4 Hz, 1H, H6 of Py). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 39.39 (dd, J_{P-P} = 117.9 Hz, J_{Rh-P} = 407.1 Hz), 60.91 (dd, J_{P-P} = 117.9 Hz, J_{Rh-P} = 407.1 Hz). FABMS: m/z = 748 (M^+ − Cl). IR (KBr tablet, cm^{-1}): ν 2020, 1604, 1096. Anal. Calcd for $C_{43}H_{37}ClNOP_2Rh$: C, 65.87; H, 4.76; N, 1.79. Found: C, 65.40; H, 4.88; N, 1.80.

Preparation of *fac*-(PCN-κ^3*P,C,N*)Rh(H)(Cl)(PCy$_3$) (4b). A mixture of [RhCl(coe)$_2$]$_2$ (51 mg, 0.071 mmol), the PN ligand (54 mg, 0.141 mmol), and PCy$_3$ (39 mg, 0.141 mmol) in toluene (1 mL) was stirred at room temperature for 3 h. After the solvent was removed in vacuo, the residue was dissolved in THF (1 mL) and then hexanes (5 mL) were added. A white precipitate was collected by removal of the solvent in vacuo and washed with a mixed solvent (30 mL) of THF and hexanes (THF/hexanes, 1:2). The residue was dried in vacuo to give **4b** as a white solid (99 mg, 87% yield). Mp: 184 °C (dec). IR (KBr tablet, cm^{-1}): ν 2063, 1602, 1099. ^{1}H NMR (300 MHz, C_6D_6): δ −16.33 (ddd, J = 8.8, 14.3, 21.5 Hz, 1H, H of Ir-H), 0.95−2.97 (m, H of PCy$_3$), 3.97 (d, J_{H-H} = 15.4 Hz, 1H, H of O-C*H*$_2$-Py), 4.12 (d, J_{H-H} = 15.4 Hz, 1H, H of O-C*H*$_2$-Py), 5.85 (d, J = 8.0 Hz, 1H), 6.20−8.41 (m, H of Ar), 10.24 (d, J = 5.5 Hz, 1H, H6 of Py). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 31.34 (dd, J_{P-P} = 111.2 Hz, J_{Rh-P} = 387.6 Hz), 61.36 (dd, J_{P-P} = 111.2 Hz, J_{Rh-P} = 387.6 Hz). FABMS: m/z = 766 (M^+ − Cl). Anal. Calcd for $C_{43}H_{55}ClNOP_2Rh$: C, 64.38; H, 6.91; N, 1.75. Found: C, 64.49; H, 6.72; N, 1.75.

Preparation of *fac*-(PCN-κ^3*P,C,N*)Rh(H)(Cl)(PBu$_3$) (4c). A toluene (3 mL) solution of PBu$_3$ (5 mg, 0.027 mmol) was added dropwise to a stirred toluene (3 mL) solution of **4a** (21 mg, 0.027 mmol). The solution was stirred at room temperature for 20 h. The solvent was removed in vacuo to give **4c** as a white powder (24 mg, quantitative yield) as a single isomer. IR (KBr tablet, cm^{-1}): ν 2065, 1603, 1097. ^{1}H NMR (300 MHz, C_6D_6): δ −16.15 (ddd, J = 12.5, 21.5, 31.5 Hz, 1H, Ir-*H*), 0.66−2.33 (m, PBu$_3$), 3.92 (d, J_{H-H} = 15.6 Hz, 1H, −O-C*H*$_2$-py), 3.99 (d, J_{H-H} = 15.6 Hz, 1H, −O-C*H*$_2$-py), 5.66−8.41 (m, arom) 10.19−10.29 (m, 1H, H6 of py). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 13.97 (dd, J_{P-P} = 115.7, J_{Rh-P} = 405.5 Hz), 58.60 (dd, J_{P-P} = 115.7, J_{Rh-P} = 405.5 Hz). FABMS: m/z = 706 (M^+ − Cl). Complete purification of **4c** for satisfaction of elemental analysis was not successful due to high solubility to solvents and its instability.

Preparation of *fac*-(PCN-κ^3*P,C,N*)Rh(H)(Cl)(PMePh$_2$) (4d). A toluene (3 mL) solution of PMePh$_2$ (6 mg, 0.032 mmol) was added dropwise to a stirred toluene (3 mL) solution of **4a** (24 mg, 0.032 mmol). The solution was stirred at room temperature for 20 h. The solvent was dried in vacuo to give **4d** as a white powder (27 mg, quantitative yield) as a single isomer. IR (KBr tablet, cm^{-1}): ν 2062, 1571, 1097. ^{1}H NMR (300 MHz, C_6D_6): δ −15.52 (ddd, J = 7.8, 11.9, 31.5 Hz, 1H, Ir-*H*), 2.16−2.23 (m, 3H, PC*H*$_3$Ph$_2$), 3.79 (d, J_{H-H} = 5.3 Hz, 1H, −O-C*H*$_2$-py), 3.81 (d, J_{H-H} = 5.3 Hz,

1H, −O-CH_2-py), 5.66−8.41 (m, arom) 9.47−9.53 (m, 1H, H6 of py). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 20.60 (dd, J_{P-P} = 127.6, J_{Rh-P} = 409.7 Hz), 58.60 (dd, J_{P-P} = 127.6, J_{Rh-P} = 409.7 Hz). FABMS: m/z = 704 (M^+ − Cl). Complete purification of **4d** for satisfaction of elemental analysis was not successful due to high solubility to solvents and its instability.

Ligand Exchange Reaction of 1b with PPh_3. To a toluene (3 mL) solution of **1b** (8 mg, 0.009 mmol) was added PPh_3 (3 mg, 0.011 mmol) at room temperature. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo to give **1a** quantitatively, which was confirmed by ^1H and ^{31}P NMR.

Ligand Exchange Reaction of 4a with PCy_3. To a toluene (6 mL) solution of **4a** (20 mg, 0.026 mmol) was added PCy_3 (7 mg, 0.026 mmol) at room temperature. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo to give **4b** along with **4a**, PPh_3, and PCy_3 (**4b**:**4a** = 80:20; the ratio was determined by ^1H and ^{31}P NMR).

Crystallographic Data Collection and Structural Determination of Complexes 1a and 4a. The crystals of **1a** and **4a** suitable for X-ray diffraction study were fixed on the end of glass fibers with cyanoacrylate adhesive and placed in a nitrogen stream at 120-(1) K. Data for **1a** and **4a** were collected by a Rigaku RAXIS-RAPID equipped with a sealed-tube X-ray generator (50 kV, 40 mA) with monochromatized Mo Kα (0.71075 Å) radiation in a nitrogen stream at 120(1) K. Indexing was performed from three oscillations, which were exposed for 90 s. The unit cell parameters and the orientation matrix for data collection were determined by the least-squares refinement. A symmetry-related absorption was corrected by use of the program ABSCOR[42] with transmission factors. Details of the data collection are summarized in Table 3.

The structure of **1a** and **4a** was solved by direct methods (SIR-97)[43] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[44] The positions of all non-hydrogen atoms of **1a** and **4a** were determined from a difference Fourier electron density map and refined anisotropically. All hydrogen atoms for each complex were placed at the calculated positions and kept fixed. All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP in Figure 2 for **1a** and Figure 3 for **4a**. Crystallographic data are collected in Table 3. Additional crystallographic data are available in the Supporting Information.

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Supporting Information Available: Detailed crystallographic data, atomic positional parameters, and bond lengths and angle for **1a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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