Syntheses and Reactions of Iridium Complexes Containing Mixed Phosphine -Olefin Ligand: (3-(Diphenylphosphino)propyl)(3-butenyl)phenylphosphine

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The reaction of [IrCl(cod)]$_2$ with ppol ligand, Ph$_2$PCH$_2$CH$_2$CH$_2$P(Ph)CH$_2$CH$_2$CH=CH$_2$, in ethanol gives an iridium complex, whose structure is converted from an ionic form, [Ir(cod)(ppol)]Cl·2C$_2$H$_5$OH (1), in polar solvents (ethanol, methanol and acetonitrile), to a molecular form, [IrCl(cod)(ppol)], in non-polar solvents (benzene and toluene). The cationic complexes, [Ir(cod)(ppol)]AsF$_6$·1/2C$_2$H$_5$OH and [Ir(cod)(ppol)]PF$_6$·1/2CH$_3$CN, were prepared to compare with the ionic form by ^{31}P NMR spectroscopy. When carbon monoxide is introduced to 1, cod is replaced by CO to give the 5-coordinated complex, [IrCl(CO)(ppol)]. Hydrogenation of 1-octene was not successful in the presence of 1. In order to verify the reason for 1 not behaving as a good catalyst for hydrogenation, electrophilic reactions with HCl, I$_2$ and HBF$_4$·etherate were performed, which yielded the oxidative addition product, [IrHCl$_2$(ppol)], the substitution product, [IrI(cod)(ppol)], and another cationic product, [Ir(cod)(ppol)]BF$_4$, respectively. Thus, the iridium complex is not sufficiently basic to activate hydrogen atoms or the olefin of the ppol ligand.

Introduction

The chemistry of transition metal complexes containing mixed phosphine-olefin ligands has been pursued to study metal catalyzed reactions of olefins.[1~7] Comparing with monodentate ligands, these chelating ligands have the advantages of stereochemical and stoichiometric control as well as stronger basicity and stability in the course of reactions. Rhodium complexes of such unsaturated tertiary phosphine ligand, Ph$_2$PCH$_2$CH$_2$CH$_2$P(Ph)CH$_2$CH$_2$CH=CH$_2$ (ppol), have been investigated and reported previously.[8] The 4-coordinated rhodium complex, [RhCl(ppol)], has been formed by the reaction of [RhCl(cod)]$_2$ with the ppol ligand and several other rhodium complexes have been prepared and characterized. In continuation of the work concerning the chemistry of the ppol ligand, iridium complexes with the same ligand show quite different chemistry from the rhodium complexes, such as coordination numbers and the bonding mode of the ppol ligand. We herein report the synthesis and various reactions of the iridium complexes of the ppol ligand.

Results and Discussion

Dependance of Structures on Solvents. Whereas the 4-coordinated RhCl(ppol) is formed by the reaction of [Rh(cod)Cl]$_2$ with ppol ligand,[8] the 5-coordinated complex [Ir(cod)(ppol)]Cl·2C$_2$H$_5$OH (1) is prepared from [Ir(cod)Cl]$_2$ and ppol in ethanol at room temperature. The infrared spectrum of 1 shows a weak band in 1550 cm^{-1} region, indicating the olefins of both ppol and cod were bonded to iridium and a broad band in 3600 cm^{-1} region due to the OH stretching vibration of the ethanol molecules. The stoichiometry that includes two ethanol molecules per iridium complex was confirmed by ^{1}H NMR spectrum and elemental analysis. The

assignment for the ^{1}H NMR spectrum of 1 in CD$_2$Cl$_2$ is as follows: δ 8.15-7.01 ppm (m, phenyl); δ 4.64 ppm (s, -OH of ethanol); δ 3.54 ppm (q, -CH$_2$ of ethanol); δ 3.32-1.27 ppm (m, -CH$_2$ of ppol and -CH$_2$ of cod); δ 1.08 ppm (t, -CH$_3$ of ethanol).

Additionally, the low intensity broad band at 3-6 ppm seems to be due to the bonded olefins of ppol and cod. Usually the protons of a bonded olefin shift upfield with a corresponding reduction in the H-H coupling constants.[9] The ^{1}H NMR data for ppol ligand in benzene-d$_6$ are: δ 7.55-6.65 ppm (m, phenyl); δ 5.9-5.4 ppm (m, -CH=); δ 5.1-4.65 ppm (m, =CH$_2$); δ 2.35-0.6 ppm (m, -CH$_2$).[10] And the ^{1}H NMR spectrum of 1,5-cyclooctadiene in CCl$_4$ gives peaks at δ 5.54 ppm for the olefinic protons and at δ 2.35 ppm for the methylene groups. Thus, coordination shift of the olefins in 1 could not be determined due to the broadness of the peak for bonded olefins. However, the ^{31}P NMR spectral data can clearly distinguish between the bonded olefin and the non-bonded olefin for the ppol ligand. The ^{31}P{^{1}H} NMR spectral data of 1 in ethanol and in benzene are presented in Table 1. The spectrum in ethanol shows two doublets. The phosphorus resonance at δ 3.5 ppm can be assigned to the central phosphorus nucleus (P$_1$) from the -PPh group of the 5.5 membered ring[11] and the resonance at δ −30.0 ppm to the terminal phosphorus atom (P$_2$) of the 6-membered ring on the basis that the phosphorus atoms in the 5.5-membered rings usually exhibit large downfield chemical shift compared to the ones of the 6-membered ring.[8,12,13] Thus, the olefin of the ppol ligand is coordinated to the metal in ethanol. On the other hand, the spectrum in benzene consists of two sets of two doublets suggesting that there are two components in solution;

δ −11.9 ppm (P$_1$); δ −27.2 ppm (P$_2$) for major component,
δ −11.4 ppm (P$_1$); δ −28.0 ppm (P$_2$) for the minor component.

Based on this data, a certain structural reorganization occurs

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Table 1. ^{31}P{^{1}H} NMR Data of [Ir(cod)(ppol)]Cl·2C$_2$H$_5$OH

Solvent	δP_1 (ppm)	δP_2 (ppm)	$^2J_{P_1-P_2}$ (Hz)
C$_2$H$_5$OH	3.5	−30.0	36.6
C$_6$H$_6$	−11.9[a]	−27.2[a]	44.5[a]
	−11.4[b]	−28.0[b]	44.5[b]

[a]Parameters for major component. [b]Parameters for minor component.

on changing the solvent from ethanol to benzene. The species present in benzene (2) is identical to the one prepared directly from the reaction of [Ir(cod)Cl]$_2$ with ppol in benzene at room temperature. The ^{31}P{^{1}H} NMR spectra of 2 in ethanol and in benzene give identical spectra to those of 1; thus, the structural reorganization between 1 and 2 is reversible.

The ratio of the major component to the minor one in benzene is 2.0. They are considered as isomers since both components have the same $^2J_{P_1-P_2}$ values (44.5 Hz) as shown in Table 1. The possible isomerization for 2 may arise from stereochemical arrangement of the phenyl group on the central phosphorus atom (P$_1$) with the chlorine atom; in one case, the phenyl group on P$_1$ in the *syn* position to the Cl, and the *anti* position in the other case. The *syn*-isomer would be the minor component since the phenyl group will experience heavier steric hindrance by the Cl atom in the *syn*-isomer than in the *anti*-isomer. The free olefin C=C stretch was observed at 1650 cm^{-1} in the infrared spectrum. Also, the ^{1}H NMR spectrum shows two broad peaks whose centers are at δ 5.54 ppm and δ 4.81 ppm due to the non-bonded olefinic group.

Therefore, 1 in ethanol is an ionic compound that all the olefins of ppol and cod are coordinated to the metal and the chloride is the anionic counterpart. On the other hand, 2 in benzene is a molecular compound that has uncoordinated olefin of ppol and the two bonded olefins of cod along with the bonded chloride. The geometry around iridium for both 1 and 2 may be either square pyramid or trigonal bipyramid. Therefore, the structural reorganization may be explained as shown in Scheme 1, and the same kind of reorganization was reported in the literature.[14]
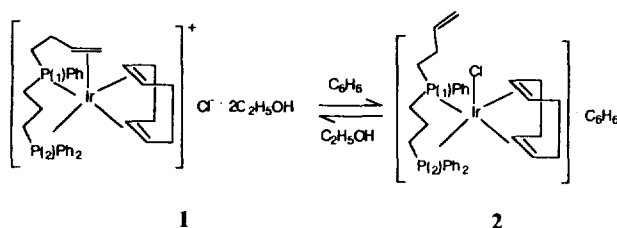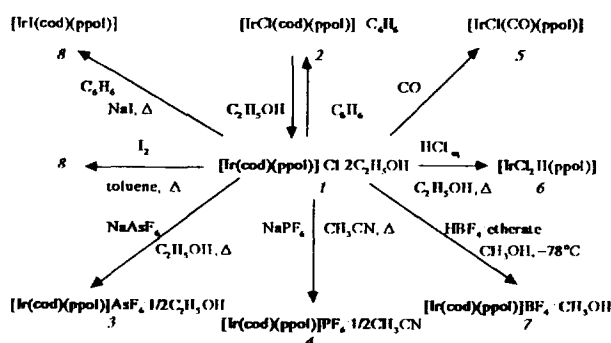
Scheme 1.

Substitution Reactions. Various reactions performed on 1 are illustrated in Scheme 2. When 1 is treated with NaI in benzene, a yellow precipitate (8) is formed; its infrared spectrum shows a non-bonded olefin absorption at 1640 cm^{-1}. The ^{31}P NMR spectrum of 8 in benzene shows a pattern similar to that of 2. This means the same type of iso-

Table 2. ^{31}P{^{1}H} NMR Data for the Cationic Complexes

Compound	Solvent	δP_1 (ppm)	δP_2 (ppm)	$^2J_{P_1-P_2}$ (Hz)
[Ir(cod)(ppol)]Cl·2C$_2$H$_5$OH	C$_2$H$_5$OH	3.5	−30.0	36.6
[Ir(cod)(ppol)] AsF$_6$·1/2C$_2$H$_5$OH	C$_2$H$_5$OH	3.2	−30.0	36.6
[Ir(cod)(ppol)] PF$_6$·1/2 CH$_3$CN	CH$_3$CN	4.4	−30.0	37.2

mers are present in 8 as in 2.

The parameters of the ^{31}P{^{1}H} nmr spectrum were: δ P$_1$ = −20.9 ppm, δ P$_2$= −38.2 ppm, $^2J_{P_1-P_2}$=44.0 Hz for the major component; δ P$_1$= −21.4 ppm, δ P$_2$= −35.5 ppm, $^2J_{P_1-P_2}$ =42.7 Hz for the minor component. The ratio of the major component to the minor one was 4.0 in this case. Thus, the ratio is larger for the iodide complex since the phenyl group on P$_1$ in he *syn*-isomer will be more sterically hindered by the bulky iodide than by chloride. Therfore, the anti -isomer is more favored in the iodide complex than in the chloride complex.

Scheme 2.

In addition, the chemical shift of the central phosphorus nucleus, δP_1, in the ^{31}P NMR spectrum supports the presence of the free olefin. When the olefinic moiety is not bonded to the metal, the P$_1$ atom is no longer a member of the 5.5-membered ring. Therefore, δP_1s for the complexes 2 and 8 are expected to be shifted upfield compared to its resonance in 1 in ethanol. Indeed, this kind of shift was observed; δP_1 for 2 is shifted upfield by ~15 ppm compared to δP_1 for 1. The same trend was observed in the rhodium complex, [Rh(ppol)$_2$]AsF$_6$, which had two ppol ligands, both containing non-bonded dangling olefins.[15] The chemical shift (δP_1) of the bonded olefin in [RhCl(ppol)] is 53.7 ppm, whereas δP_1 of the non-bonded olefin in [Rh(ppol)$_2$]AsF$_6$ is −8.0 ppm. Thus, both olefins of cod are bonded to iridium but the olefin of ppol is not coordinated.

The chloride anion in 1 can be replaced ,by other anions, such as PF$_6^-$ and AsF$_6^-$. A white crystalline solid, [Ir(cod)(ppol)] AsF$_6$·1/2C$_2$H$_5$OH (3), is isolated by adding NaAsF$_6$ to 1 in ethanol. The infrared spectrum of 3 shows the presence of AsF$_6$ whoseabsorptions contain a strong band at 696 cm^{-1} and a shoulder at 672 cm^{-1} and ethanol molecules in the crystal lattice.[16] Additionally, a weak absorption at 1970 cm^{-1} is observed. This peak might be due to a small amount of a carbonyl impurity; this point will be discussed in the later part of this paper.

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When acetonitrile is used as a solvent for the reaction of **1** with NaPF$_6$, a white solid, [Ir(cod)(ppol)] PF$_6$·1/2 CH$_3$CN (**4**), is produced. The absorption bands at 845 cm^{-1} and 559 cm^{-1} in the infrared spectrum are due to PF$_6^-$ anion and a weak band at 2270 cm^{-1} is for the acetonitrile in the lattice and the elemental analysis confirms the presence of acetonitrile. The ^{31}P NMR spectral data of **1, 3** and **4** are presented in Table 2. The observed similarity in the ^{31}P NMR spectra for those three compounds suggests that the species in ethanol or acetonitrile have similar structures. The molar conductivities of **3** (61.0 ohm^{-1} cm^{-2} mol^{-1} in ethanol) and **4** (137.0 ohm^{-1} cm^{-2} mol^{-1} in acetonitrile) shows that both **3** and **4** are 1:1 electrolytes.[17]

As mentioned earlier, a weak absorption band at 1970 cm^{-1} was observed in the IR spectrum of each cationic complex, *i.e.*, **1, 3** and **4**. This band might be due to a small amount of a carbonyl impurity. Abstraction of CO from alcohols with basic and bulky phosphines has been reported previously.[18~21] To confirm that the 1970 cm^{-1} band is due to the CO stretch, the carbonyl complex, [IrCl(CO)(ppol)], (**5**), was prepared by bubbling CO gas through an ethanol solution of **1**. An absorption band at 1970 cm^{-1} in the infrared spectrum of **5** supports the presence of carbonyl complex in the cationic complexes. There is a weak absorption at 1530 cm^{-1} and no free C=C absorption in the infrared spectrum, indicating that the olefin is bonded to the metal. Both the elemental analysis and the effective atomic number rule suggest the cod ligand to be replaced by CO, thus, the complex **5** would be 5-coordinated. However, it cannot be decided only by the carbonyl stretching frequency whether the complex has a square pyramidal or a trigonal bipyramidal structure. Due to the extremely low solubility of the carbonyl complex in various solvents, no signicant ^{31}P NMR data could be obtained even after ~30,000 scans.

Electrophilic Reactions. The iridium complex, **1**, might be considered as a good candidate for a hydrogen catalyst since the olefin end of the ppol ligand could be activated under ambient conditions to react with molecular hydrogen to form an alkane and generate a vacant coordination site.[10] However, the hydrogenation of 1-octene in the presence of **1** was not successful after 48 hours of reaction at 1 atm. of hydrogen.

Before trying at higher pressure of hydrogen, we decided to perform the reactions with several electrophiles such as HCl, I$_2$ and HBF$_4$·etherate to attack the olefin part of the ppol ligand. The reaction product (**6**) of **1** with conc. HCl gives an Ir-H absorption at 2250 cm^{-1} in the infrared spectrum. The M-H stretching frequencies are sensitive to other substituents in the metal complex, particularly to the ligands in positions *trans* to hydrogens. The observed value is in the range quoted for H trans to Cl in octahedral hydrido-iridium(III) complexes.[22,23] The ^{31}P NMR spectrum of this compound in acetonitrile gives the following data: δ P$_1$= −13.5 ppm; δ P$_2$= −25.3 ppm; $^2J_{P^1-P_2}$=26.2 Hz. Since the $^2J_{PP}$ values of Ir(I) complexes are known to be in the range of 15-30 Hz and the $^2J_{PP}$ values of Ir(III) complexes vary from 15 to 35 Hz, one cannot tell whether the oxidation state of this compound is I or III, at this point. The ^{31}H NMR of **6** shows a doublet of doublets at −15.3 ppm, which confirms the presence of a hydride, and this chemical shift

is close to the values found for H trans to Cl in IrHCl$_2$(bdpps) (bdpps=2,2'-bis(diphenyl-phosphino)stilbene and IrHCl$_2$(CO)(PR$_3$)$_2$.[24] A ^{1}H{^{31}P} NMR spectrum gives a single peak at the same position. By selective decoupling of a phosphorus nucleus at a time, the each coupling constant for another nucleus with the hydride ligand was obtained: $^2J_{P_1-H}$=12.7± 1.0 Hz; $^2J_{P_2-H}$=8.3± 1.0 Hz. Since these coupling constants are in the range expected for two-bond *cis* -coupling constant between phosphorus and hydride, the hydride in **6** is *cis* to both phosphorus nuclei.[24] Elemental analysis for **6** indicates that two chlorine atoms are included. Thus, the oxidation number of iridium is III, which gives the molecular formula, IrCl$_2$H(ppol), for **6**. Thus, HCl adds oxidatively to iridium to give a 6-coordinate octahedral geometry, and the cod ligand is displaced in this reaction.

The reaction of **1** with I$_2$ was attempted to find out if iodination gives a similar result to the HCl reaction that was mentioned above. However, ^{31}P NMR the spectrum of the product, which was obtained after refluxing with I$_2$ for two hours in toluene, is identical to that of [IrI(cod)(ppol)]. Therefore, iodine does not oxidatively add to the iridium(I) complex; instead, it gives only the halogen substitution product.

Protonation of **1** with HBF$_4$·etherate was attempted at −78 ℃ in methanol. However, the ^{31}P NMR spectrum shows that simply the chloride anion is displaced by the BF$_4^-$ anion to give the another cationic complex, [Ir(cod)(ppol)]BF$_4$ (**7**). The infrared spectrum of **7** contains no band for Ir-H stretching but a very strong and broad band at ~1050 cm^{-1} due to the BF$_4^-$. The ^{31}P{^{1}H} nmr spectrum in CH$_3$OH, which is similar to those observed for the other cationic complexes, **1, 3** and **4**, gives the following data: δ P$_1$=3.5 ppm, δ P$_2$= −30.4 ppm and $^2J_{P-P}$=37.2 Hz. The data indicates that the protonation of olefin of the ppol ligand in the iridium complex (**1**) does not occur but the substitution product (**7**) is obtained. It is because the iridium complex (**1**) is not sufficiently basic to activate the olefinic moiety of ppol as Crabtree and his coworkers[4] reported for the reaction of [Ir(cod)L$_2$]PF$_6$ (L=PPh$_3$, PMePh$_2$) with HPF$_6$. Therefore it is concluded that the electrophiles such as HCl, I$_2$ and HBF$_4$·etherate can not affect the olefinic moiety in the iridium complex (**1**) at all due to the insufficient basicity of the metal complex and that is the reason why the iridium complex in this work can not act as a good catalyst.

Experimental

Materials. Iridium trichloride trihydrate (IrCl$_3$·3H$_2$O) was purchased from Engelhard Industries, Newark, New Jersey. All reagent-grade solvents were dried by distillation over appropriate drying agents under nitrogen or by the freeze-thaw method prior to use. All other chemicals and reagents were reagent-quality and were used without further purification.

Physical Measurements. Infrared spectra were measured on a Perkin Elmer 337 grating spectrophotometer from 400 to 4000 cm^{-1} as nujol mulls between potassium bromide plates. Conductance measurements were made on an Industrial Instruments Ins. Conductivity 7Bridge Model RC 16B2 operating at 1000 c.p.s. Proton magnetic resonance spectra

were collected on a a Bruker HX90 spectrometer with tetra-methylsilane as an internal standard, in general. Fourier-mode, proton-noise-decoupled, phosphorus-31 NMR spectra were collected on a Bruker HX90 spectrometer operating at 36.43 MHz, with a Bruker B-NC 12 data system. Phosphoric acid (85%) was used for an external refernce and positive chemical shifts are measured downfield from phosphoric acid. Mass spectra were measured on an AEI-MS902 spectrometer at an ionizing energy of 70 eV by Dr. Weisenberger at the Ohio State University. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona, USA and KIST, Seoul, Korea.

(3-(Diphenylphosphino)propyl)(3-butenyl)phenyl-phosphine (ppol). The ppol ligand was prepared according to the literature method.[8]

[Ir(cod)(ppol)] Cl·2C₂H₅OH (1). A solution of [IrCl(cod)]₂ (0.64 g, 2.00 mmol) in absolute ethanol (25 mL) was treated with ppol (4.0 mL; 0.5271 M in benzene) and the mixture was stirred at room temperature for one hour. The resultant pale yellow solution was evaporated almost to dryness under vacuum; a white precipitate was separated after diethyl ether (30 mL) was added to the solution, The product was washed with diethyl ether and dried *in vacuo*

Analysis for C₃₇H₅₀ClIrO₂P₂: Calcd: C, 54.58; H, 6.11; Cl, 4.28. Found: C, 54.48; H. 5.98; Cl, 4.37.

[IrCl(cod)(ppol)]·C₆H₆ (2). To a solution of [IrCl(cod)]₂ (0.32 g; 0.48 mmol) in benzene (20 mL) was added ppol (2.3 mL; 0.478 M in benzene) and the solution was stirred at room temperature for one hour. After evaporating most of the solvent, hexane (30 mL) was added to isolate a pale yellow solid. The product was washed with hexane and dried *in vacuo.*

Analysis for C₃₉H₅₈ClIrP₂: Calcd: C, 58.20; H, 5.72; Cl, 4.41. Found: C, 58.07; H, 5.59; Cl, 4.26.

[Ir(cod)(ppol)] AsF₆·1/2C₂H₅OH (3). A solution of [IrCl(cod)]₂ (0.28 g; 0.42 mmol) in ethanol (20 mL) was treated with ppol (2.0 mL; 0.478 M in benzene). To this was added a boiling ethanol solution of NaAsF₆ (0.19 g; 0.90 mmol) and the resultant mixture was 8refluxed for one hour. After cooling, a white solid was separated. The product was washed with water and diethyl ether and dried *in vacuo.*

Analysis for C₃₄H₄₃AsF₆IrO₀.₅P₂: Calcd: C, 45.26; H, 4.75; F, 12.63. Found: C, 45.58; H, 4.82; F, 12.78.

[Ir(cod)(ppol)] PF₆·1/2CH₃CN (4). To a solid mixture of 1 (0.30 g; 0.37 mmol) and NaPF₆ (0.08 g; 0.48 mmol) was added acetonitrile (20 mL). The mixture was refluxed for 30 min. A crystalline white solid was separated during the refluxing. After cooling, the productwas collected on a Schlenk frit and washed with water. The sample was then washed with diethyl ether and dried *in vacuo.*

Analysis for C₃₄H₄₁·5F₆IrN₀.₅P₃: Calcd: C, 47.61; H, 4.90; N, 0.82. Found: C, 47.46; H, 5.06; N, 0.85.

[IrCl(CO)(ppol)] (5). A 0.20 g sample of 1 was dissolved in 20 mL of ethanol and CO was bubbled through the solution for 20 min. The solvent was evaporated to 5 mL by bubbling both CO and N₂ through the solution, then diethyl ether was added to help precipitation of a solid. The solution was allowed to stand several days and white crystals formed. The crystals were collected on a Schlenk frit, washed with diethyl ether and dried with a gaseous mixture of CO

and N₂.

Analysis for C₂₆H₂₈ClIrOP₂: Calcd: C, 48.30; H, 4.33; Cl, 5.50. Found: C, 48.01; H, 4.58; Cl, 5.78.

[IrCl₂H (ppol)] (6). To a solution of 1 (0.25 g; 0.31 mmol) in 20 mL of ethanol was added concentrated aqueous HCl (0.5 mL) and the mixture was refluxed for one hour. After cooling, the solvent was evaporated to 3 mL under vacuum and diethyl ether (20 mL) was added. The solution was kept in a refrigerator overnight. A resultant white precipitate was washed with ether and dried in vacuo.

Analysis for C₂₅H₂₉Cl₂IrP₂: Calcd: C, 45.87; H, 4.43; Cl, 10.85. Found: C, 45.82; H, 4.61; Cl, 10.61.

[Ir(cod)(ppol)] BF₄·CH₃OH (7). To a solution of 1 (0.32 g) in methanol (20 mL) at −78 ℃ was added HBF₄·etherate (1 mL). A white solid formed immediately; the resultant mixture was stirred for one hour at the same temperature. After filtration, the product was washed with ether and dried *in vacuo.*

Analysis for C₃₄H₄₄BF₄IrOP₂: Calcd: C, 50.62; H, 5.46; F, 8.93. Found: C, 50.28; H, 5.32; F, 8.69.

[IrI(cod)(ppol)] (8). A mixture of 1 (0.20 g; 0.24 mmol) and NaI (0.05 g; 0.33 mmol) in benzene (20 mL) was refluxed for one hour. The pale yellow precipitate was collected on a Schlenk frit, washed with water and diethyl ether, in sequence, and dried *in vacuo.*

Reaction of 1 with I₂. To a solution of 1 (0.30 g; 0.37 mmol) in toluene (10 mL), was added I₂ (0.30 g; 1.2 mmol) and the mixture was refluxed for two hours. Unreacted iodine was filtered off and the solution was evaporated to dryness to obtain a yellow solid. All the spectral data were identical to **8.**

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Hydrogenation of Arenes with Metallic Iridium and Rhodium Powders Prepared from Iridium(I) and Rhodium(I)-COD Complexes under Mild Conditions

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Metallic iridium and rhodium powders prepared from the reactions of $[M(COD)(PhCN)_2]ClO_4$ (M = Ir(1), Rh(2); COD = 1,5-cyclooctadiene) with hydrogen at room temperature in methylene chloride show catalytic activities for hydrogenation of arenes at room temperature under atmospheric pressure of hydrogen. Most substituents (CH_3, COOH, NO_2, CH_2OH, CHO, OPh, OCH_3, C=C, halogens and CH_2Cl) on aromatic ring suppress the rate of the hydrogenation of the aromatic ring while the aromatic ring hydrogenation of phenol and 1,4-dihydroxobenzene is faster than that of benzene over these metallic powders. Hydrogenation of benzoic acid occurs only at the aromatic ring leaving the COOH group intact over iridium metal powders while benzoic acid is not hydrogenated at all over rhodium metal powders. Carbonyl, nitro, acetylenic and olefinic groups on an aromatic ring are hydrogenated prior to the aromatic ring hydrogenation. Hydrogenolysis of OH groups of phenol, benzyl alcohol and 1,4-dihydroxobenzene, and hydrodehalogenation of halobenzenes, benzyl halides and cinnamyl chloride also occur along with the hydrogenation of aromatic ring.

Introduction

Metallic powders and metal oxides are somewhat common heterogeneous catalysts.[1] Unsupported metallic catalysts are usually prepared by the reduction of metal compounds at high temperature under hydrogen mostly in the absence of a solvent or soaking in solution.[2] The characteristics of the unsupported metal surfaces have been recently investigated,[3-7] and only a few reports have been made for the catalysis with unsupported metal powders[2,8,9] while supported metallic catalysts are widely studied probably because they show high reactivities for small molecules such as CO, H_2, O_2, ethylene and other organic compounds.[2,10~14]

Rhodium[15] and iridium[3,8,16] metallic powders have been generally obtained by the reduction of their chloride salts, $M(III)Cl_3$ (M = Rh, Ir) under hydrogen at high temperature. Whitesides reported that platinum black is produced from the reaction of Pt(II)-COD (COD = 1,5-cyclooctadien) complexes.[9] Crabtree observed that Ir(I)-COD complexes under catalytic hydrogenation conditions show a strong resemblance to heterogeneous catalysts such as colloidal metallic iridium.[17,18]

Catalytic hydrogenation of arenes and heteroarenes has

been studied with soluble metal compounds[19,20] and heterogeneous catalysts[1,21] such as metal powders, metal oxides, and supported metal complexes. Only one report, to our knowledge, has been made for the hydrogenation of benzene with iridium metal powders supported on metal oxides that were prepared under hydrogen at high temperature,[16b] while extensive studies have been carried out for the hydrogenation of arenes with various metal powders supported and unsupported.[1,19,21]

During the investigation of reactions of Ir(I)-COD complexes,[22] we found that solutions of $[M(COD)(PhCN)_2]ClO_4$ (M = Ir(1), Rh(2)) under atmospheric pressure of hydrogen rapidly produce fine particles of iridium and rhodium metal at room temperature. This observation prompted us to look into the catalytic activities of these metal powders, and the hydrogenation of arenes was chosen to be investigated since iridium metal powders have never been extensively studied for their catalytic activities for the hydrogenation of arenes with various types of substituents. Iridium and rhodium metal powders (prepared under the same experimental conditions) show some differences in their catalytic activities, which are also included in this report.