

Preparation, Reactions and Catalytic Activities of Water Soluble Iridium-Sulfonated Triphenylphosphine Complex

Chong Shik Chin*, Won-Tae Chang, Seokyeon Yang, and Kwang-Suk Joo

Department of Chemistry, Sogang University, Mapo-gu, Seoul 121-742, Korea

Received January 11, 1997

Water soluble iridium complex, $\text{IrCl}(\text{CO})(\text{TPPTS})_2 \cdot x\text{H}_2\text{O}$ (**1**) (TPPTS=*m*-trisulfonated triphenylphosphine) has been prepared from the reaction of a water soluble complex, $\text{IrCl}(\text{COD})(\text{TPPTS})_2 \cdot 6\text{H}_2\text{O}$ (COD=1,5-cyclooctadiene) with CO and unambiguously characterized by electronic absorption, ^{31}P NMR, ^{13}C NMR and IR spectral data. Complex **1** catalyzes the hydration of terminal alkynes to give ketones in aqueous solutions at room temperature. The rate of $\text{PhC}\equiv\text{CH}$ hydration dramatically increases with addition of MeOH to the reaction mixture in H_2O , which is understood in terms of i) the excellent miscibility between H_2O and MeOH and ii) the assumed catalytic hydration pathway involving the initial formation of $(\text{alkyne})\text{IrCl}(\text{CO})(\text{TPPTS})_2$.

Introduction

Metal catalyzed organic reactions in aqueous solutions have been relatively rarely studied, while they have several advantages over those in organic solvents,¹⁻³ probably because it is somewhat cumbersome to prepare water-soluble metal complexes. Sulfonation of phenyl groups of arylphosphines seems to be a very common preparative method of water soluble ligands and metal complexes.²⁻⁵ Water (as a reactant) involved reactions, when they are catalyzed by water soluble catalysts, deserve an investigation for the efficiency in aqueous solutions and comparison with the data by water insoluble metal complexes. Alkyne hydration is known to occur in the presence of strong oxidizing reagents⁶ and transition metal complexes.⁷ To the best of our knowledge, no detailed report has been made for the hydration of alkynes with water soluble metal complexes of sulfonated tertiary phosphines except a brief statement about acetylene hydration with rhodium- and ruthenium-sulfonated triphenylphosphine.⁸

We now wish to report synthesis and reactions of a water soluble four-coordinated iridium complex, $\text{IrCl}(\text{CO})(\text{TPPTS})_2 \cdot x\text{H}_2\text{O}$ (**1**, TPPTS= $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$) and its catalytic activities for hydration of alkynes to give ketones in aqueous solutions at room temperature.

Results and Discussion

Synthesis. Water soluble complex, $\text{IrCl}(\text{CO})(\text{TPPTS})_2 \cdot x\text{H}_2\text{O}$ (**1**) has been prepared by replacing COD (1,5-cyclooctadiene) of $\text{IrCl}(\text{COD})(\text{TPPTS})_2 \cdot 6\text{H}_2\text{O}$ (**2**)⁴ with CO (eq. 1). Reaction of **2** with CO in H_2O initially produces a complex containing more than one CO (according to infrared spectra) and refluxing the solution of this unknown complex for 24 hours gives complex **1** (see Experimental for details). Complex **1** has been unambiguously characterized by electronic absorption, ^{31}P NMR, ^{13}C NMR and infrared spectral measurements. It is well-known that Vaska's complex, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (**3**) and related four coordinated iridium(I) complexes show three prominent absorption bands in the visible region.⁹ The product, **1** prepared in this study shows three bands very similar to those of **3** (see Fig-

ure 1). One signal (δ 28.83 ppm) observed for ^{31}P NMR of **1** unambiguously suggests $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ where the two TPPTS should be *trans* to each other. A triplet (δ 171.4, $J_{\text{P-C}}=8.0$ Hz, CO) measured for ^{13}C NMR also indicates two TPPTS being *cis* to CO. ^1H NMR spectra in D_2O (100% deuterium) suggest 6-12 H_2O molecules in a molecule of **1** depending on drying time and temperature. The $\nu_{\text{C=O}}$ (1964 cm^{-1}) measured for **1** is close to those of $\text{IrCl}(\text{CO})(\text{PPh}_2(m\text{-C}_6\text{H}_4\text{SO}_3))_2$ (1960 cm^{-1})⁸ and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (1961 cm^{-1}).¹⁰ It is certain, according to infrared spectral data that compound **1** contains a number of H_2O molecules. Elemental analysis data are insufficient to determine the number of

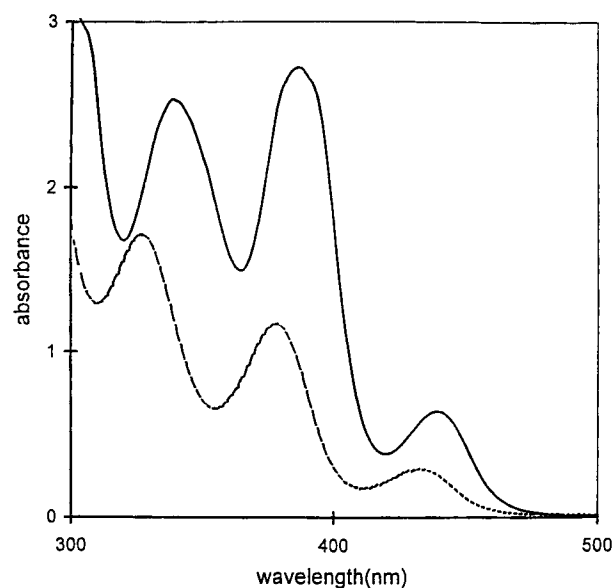
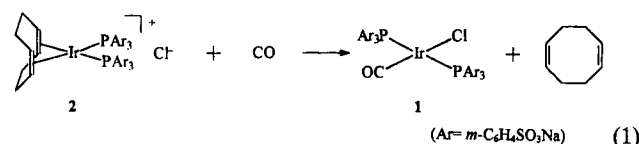


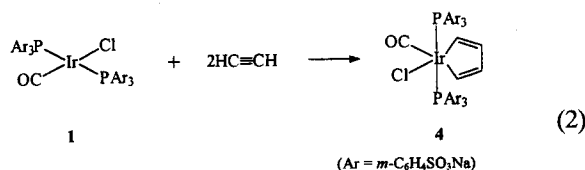
Figure 1. Electronic absorption spectra of $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**1**, 1.0×10^{-3} M) in D_2O (---) and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (**3**, 1.0×10^{-3} M) in C_6H_6 (—).

H₂O molecules in 1.

Reactions. Complex **1** seems to react with CH₂=CHCN in a similar manner as the non-sulfonated phosphine (PPh₃) complex (**3**) does. One of the characteristics of **3** is the rapid formation of (CH₂=CHCN)IrCl(CO)(PPh₃)₂ (**3a**)¹¹ where CH₂=CHCN is coordinated through the π-system of the olefinic group. Complex **1** also reacts immediately with CH₂=CHCN to give a beige product which is tentatively identified as the adduct, (CH₂=CHCN)IrCl(CO)(TPPTS)₂·xH₂O (**1a**) by comparison with the data for **3a** (see below). Both of **1a** and **3a** show no absorption band in the visible region, which is a well-known observation for the olefin adducts of the related four coordinated iridium complexes.¹¹ The ν_{C=O} and ν_{C=N} are observed at 2024 and 2238 cm⁻¹ for PPh₃ complex **3a**¹¹ and at 2054 and 2240 cm⁻¹ for TPPTS complex **1a**. The ¹H NMR signals for CH₂=CHCN in **3a** are shown at δ 0.25 (m, 1H), 2.42 (m, 1H), 4.35 (m, 1H). It should be mentioned that complex **3a** has not been isolated in high purity since weak infrared absorption bands were also measured at 2006 and 1977 cm⁻¹ for the samples of **3a**.

Complex **1** instantly reacts also with H₂ (1 atm) in H₂O at 25 °C to give unidentified product(s) which seems to be different, according to ¹H NMR and IR spectral data (see data in Experimental), from the PPh₃ analogue Ir(H)₂Cl(CO)(PPh₃)₂¹¹ obtained from the reaction of **3** with H₂.

Complex **1** readily reacts with HC≡CH at 0 °C to produce a iridacyclopentadiene **4** (eq. 2) identified by ¹H-, ¹³C- and ³¹P NMR and IR spectral data (see Experimental). At 25 °C, the reaction of **1** with HC≡CH is very rapid and gives unidentified product(s) whereas the PPh₃ analog complex **3** does not react with HC≡CH. The well-defined signals due to the metallacycle moiety of Ir-CH=CH-CH=CH in [Ir-CH=CH-CH=CH(CO)(PhCN)(PPh₃)₂]⁺ and related complexes^{12,13} are all clearly seen in the ¹H- and ¹³C NMR spectra of **4** (see data in Experimental).



Catalytic Hydration of Alkynes. Terminal alkynes readily undergo hydration to give ketones in the presence of **1** at 25 °C under N₂ (eq. 3). The hydration does not occur in the presence of TPPTS only (*i.e.*, in the absence of **1**) and occurs very slowly in the presence of the other water soluble complex, IrCl(COD)(TPPTS)₂·6H₂O. The hydration of unsubstituted HC≡CH is much faster than those of alkynes with substituents (see Table 1) probably due to steric hindrance of the substituents against the interaction between alkynes and iridium in **1**. Catalytic activity of **1** does not seem to deteriorate at least for the first 10 hours, then slowly decrease and persist even after a week. For example, turnover numbers (alkyne/Ir/hr) were found to be 0.75, 0.75, 0.39, 0.3 and 0.20 after 6, 10, 24, 48 and 96 hours, respectively for hydration of PhC≡CH in H₂O (see Table 2 for experimental conditions).

As shown in Table 1 and 2, the hydration occurs most ra-

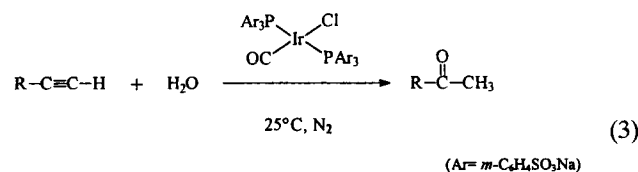
Table 1. Hydration of Alkynes (1.0 × 10⁻⁴ mol) in the Presence of IrCl(CO)(TPPTS)₂·xH₂O, **1** (3.3 × 10⁻⁵ mol) in Aqueous Solutions at 25 °C for 24 Hours under N₂

| Alkyne | Solvent (mL) | Product (%) |
|---|--|--|
| PhC≡CH | H ₂ O (1.0) | PhC(O)CH ₃ (31) |
| | H ₂ O (0.5), MeOH (0.5) | PhC(O)CH ₃ (100) ^b |
| | H ₂ O (0.5), THF (0.5) | PhC(O)CH ₃ (39) ^b |
| | H ₂ O (0.5), CH ₃ CN (0.5) | PhC(O)CH ₃ (trace) ^b |
| | | |
| HC≡C(CH ₂) ₄ C≡CH | H ₂ O (1.0) | CH ₃ C(O)(CH ₂) ₄ C≡CH (27) |
| | H ₂ O (0.1), MeOH (0.9) | CH ₃ C(O)(CH ₂) ₄ C≡CH (33) CH ₃ C(O)(CH ₂) ₄ C(O)CH ₃ (3) |
| HC≡C(CH ₂) ₄ CH ₃ | H ₂ O (1.0) | CH ₃ C(O)(CH ₂) ₄ CH ₃ (49) |
| CH ₃ OCH ₂ C≡CH | H ₂ O (1.0) | CH ₃ OCH ₂ C(O)CH ₃ (10) |
| HC≡CCH ₂ Cl | H ₂ O (1.0) | CH ₃ C(O)CH ₂ Cl (15) |
| | | CH ₃ C(O)CH ₃ (13) |
| HC≡CH | H ₂ O (1.0) | CH ₃ CHO (0.03 mol) ^c |
| PhC≡CPh ^a | H ₂ O (1.0), MeOH (1.0) | PhC(O)CH ₂ Ph (3) |
| | | <i>cis</i> -PhCH=CHPh (20) <i>trans</i> -PhCH=CHPh (7) |

^a At 100 °C. No reaction takes place at room temperature. ^b After 4 hours. ^c Total amount of CH₃CHO produced under 1 atm of HC≡CH.

Table 2. Rates of PhC≡CH (3.3 × 10⁻³ mol) Hydration for the First 2 Hours with IrCl(CO)(TPPTS)₂·xH₂O, **1** (3.3 × 10⁻⁵ mol) at 25 °C under Nitrogen

| Solvent (mL) | PhC(O)CH ₃ /Ir/Hr |
|------------------------------------|------------------------------|
| H ₂ O (1.0) | 0.75 |
| H ₂ O (0.7), MeOH (0.3) | 22.5 |
| H ₂ O (0.5), MeOH (0.5) | 24.3 |
| H ₂ O (0.3), MeOH (0.7) | 25.7 |
| H ₂ O (0.2), MeOH (0.8) | 22.8 |
| H ₂ O (0.1), MeOH (0.9) | 49.0 |
| H ₂ O (0.2), MeOH (1.8) | 47.4 |



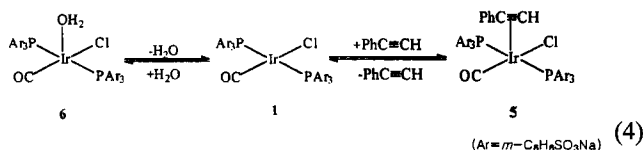
pidly in the presence of MeOH which seems to be the best solvent for the reaction (eq. 3). The higher reaction rate in the presence of MeOH than those in the presence of other organic solvents (see Table 1) may be due to excellent miscibility between H₂O and MeOH since the mixture of H₂O and MeOH dissolves all the materials (catalyst **1**, reactant alkynes, product ketones) into a homogeneous solution while organic layers were always separated from the aqueous layer containing catalyst when THF and CH₃CN were used as solvents.

In order to obtain more information on the higher rates in H₂O/MeOH, the hydration of PhC≡CH (3.3 × 10⁻³ mol) was carried out in MeOH (1 mL) containing only 0.1% H₂O (*ca.* 5 × 10⁻⁴ mol). A small amount of hydration pro-

duct, PhC(O)CH_3 ($<3 \times 10^{-4}$ mol) was produced in the early stage of the reaction and then no additional PhC(O)CH_3 was measured. We found instead a significant amount of $\text{PhC(CH}_3\text{)(OCH}_3\text{)}_2$ and a very small amount of $\text{PhC(OCH}_3\text{)=CH}_2$, both of which seem to be slowly produced. These two methoxy compounds are certainly the products of the reaction of $\text{PhC}\equiv\text{CH}$ with MeOH. Both $\text{PhC(CH}_3\text{)(OCH}_3\text{)}_2$ and $\text{PhC(OCH}_3\text{)=CH}_2$ are slowly converted into PhC(O)CH_3 when H_2O is added into the reaction mixture. These observations suggest that PhC(O)CH_3 is produced mainly from the direct hydration of $\text{PhC}\equiv\text{CH}$ with H_2O in $\text{H}_2\text{O/MeOH}$ solutions.

The higher rates of hydration in lower concentration of H_2O (see Table 2) may be explained by higher concentration of the intermediate, π -alkyne complex (**5** in eq. 4) assuming that i) H_2O and $\text{PhC}\equiv\text{CH}$ competitively coordinate to **1** to give **6** and **5** (eq. 4) and ii) the hydration (eq. 3) occurs through the most likely reaction pathway⁷ where the π -alkyne complex such as **5** is initially formed and subsequently H_2O molecule attacks the coordinated alkyne. Accordingly, the rate decrease in $\text{H}_2\text{O/CH}_3\text{CN}$ solution (see Table 1) is probably due to the coordination of the fairly good ligand, CH_3CN to iridium inhibiting the formation of **5**.

Diphenylacetylene does not undergo the hydration in the presence of **1** in aqueous solution at 25 °C. At 100 °C in MeOH/ H_2O , however, a small amount of the hydration product, $\text{PhC(O)CH}_2\text{Ph}$ was found with a large amount of PhCH=CHPh (see Table 1). It may not be so surprising to see the hydrogenation products, *trans*- and *cis*- PhCH=CHPh since alcohols have been known as good hydrogen donors to unsaturated substrates in the presence of related metal complexes.¹⁴ The production of PhCH=CHPh is very slow in MeOH in the absence of H_2O , which may be due to the very poor solubility of **1** in MeOH.



Addition of MeOH shows a little effect on the rate of the hydration of diyne $\text{HC}\equiv\text{C(CH}_2\text{)}_4\text{C}\equiv\text{CH}$ (see Table 1). Hydration of alkynes such as $\text{HC}\equiv\text{CC(CH}_3\text{)}_3$, $\text{HC}\equiv\text{CC(CH}_3\text{)}_2\text{NH}_2$, $\text{HC}\equiv\text{CC(O)OC}_2\text{H}_5$ and $\text{HC}\equiv\text{CC(CH}_3\text{)}_2\text{OH}$ is too slow to be measured in the presence of **1** at 25 °C in aqueous solutions. Relative rates observed for different alkynes (see Table 1) may be due to various reasons including stereochemical as well as electronic effects between the catalyst and alkynes. Further investigation is currently being carried out to obtain more information on these observations.

Finally, it may be mentioned that complex **1** also catalyzes the double bond migration of allylic alcohols to give ketones in aqueous solutions at 25 °C. The double bond migration by **1**, however, is too slow to observe the intermediates, enols¹⁵ while significant amounts of the enols have been measured in the double bond migration of allylic alcohols catalyzed by the other water soluble complex, of $\text{IrCl(COD)(TPPTS)}_2 \cdot x\text{H}_2\text{O}$, **2**.¹⁶

Experimental

Instrumentation. ^1H -, ^{13}C - and ^{31}P NMR spectra were measured either with Varian Gemini 200 or 300 MHz spectrometer. Electronic and infrared absorption spectra were obtained by Shimadzu IR-440 and UV-240 spectrophotometers, respectively. Elemental and GC/mass analyses were carried out by Carlo Erba EA1108 and Varian 3700 (or Hewlett Packard HP5890A)/VG Trio 2000 at Organic Chemistry Research Center, Sogang Univ.

Synthesis. *m*-Trisulfonated triphenylphosphine, TPPTS ($\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$). This was prepared as described below by somewhat modified method of the reported procedure.³ Fuming H_2SO_4 (oleum, 60 mL, SO_3 , 65%) was slowly added into the triphenylphosphine (10 g, 3.8×10^{-2} mol) in H_2SO_4 (60 mL, 97%) on ice bath to observe the reaction mixture solution turning pale yellow. The reaction mixture was warmed up to room temperature and stirred for 24 hours. Unreacted SO_3 gas was removed by nitrogen bubbling before it was poured into a 200 mL of d- H_2O at 0 °C slowly enough to maintain the reaction mixture at ca. 10 °C. Excess H_2SO_4 and $-\text{SO}_3\text{H}$ (of $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{H})_3$) in the reaction mixture were neutralized by NaOH (190 g of NaOH in 200 mL of H_2O) using pH-paper on ice bath. MeOH (1.5 L) was added and white insoluble Na_2SO_4 was removed by filtration. To the filtrate, EtOH (ca. 4 L) and Et_2O (ca. 4 L) were added to precipitate the white product, TPPTS which was isolated by filtration. Addition of H_2O (30 mL), MeOH (1.5 L) and removal Na_2SO_4 were repeated once more. The ^{31}P NMR spectrum in D_2O of the product showed that it contained 95% of $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ (δ -5.20 ppm) and 5% of $\text{O}=\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ (δ 35.19 ppm). This crude product was recrystallized three times using water (20 mL) and ethanol (1.2 L) to obtain the reagent grade of $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ (>95%). The final yield was 15.4 g or 65% based on TPPTS.

$\text{IrCl(CO)(TPPTS)}_2 \cdot x\text{H}_2\text{O}$ (1**).** The reddish orange MeOH (25 mL) solution of $\text{IrCl(COD)(TPPTS)}_2 \cdot 6\text{H}_2\text{O}$ (0.77 g) turned colorless within two minutes under CO (1 atm) at room temperature. Refluxing this colorless solution for 24 hours produced a small amount of yellow solid (**1**) in a yellow solution which gave more yellow micro-crystals of **1** upon cooling on ice bath under N_2 after being reduced to ca. 15 mL by evaporation. The product was isolated by filtration and washed with cold methanol and dried under vacuum for 24 hours to obtain 0.56 g of $\text{IrCl(CO)(TPPTS)}_2 \cdot x\text{H}_2\text{O}$. Found: C, 28.04; H, 2.54. Calcd. for $\text{IrClO}_{25}\text{P}_2\text{C}_{37}\text{H}_{36}\text{S}_6\text{Na}_6$ (for $\text{IrCl(CO)(TPPTS)}_2 \cdot 6\text{H}_2\text{O}$): C, 29.58; H, 2.42. ^1H NMR (D_2O , 25 °C) δ 7.7-8.1 (m, C_6H_4); ^{31}P NMR (D_2O , 25 °C) δ 28.83; ^{13}C NMR (D_2O , 25 °C) δ 171.4 (t, $J_{\text{P-C}}=8.0$ Hz, CO), 132-147 (C_6H_4); IR (Nujol) $\nu_{\text{max}}/\text{cm}^{-1}$ 1964s ($\text{C}\equiv\text{O}$), 1040s, 1145s, 1220s, br. (SO_3), 1650br, 3400s, br. (H_2O); electronic absorption (H_2O , 25 °C) λ_{max} (nm) 440, 388, 340 (see Figure 1).

Reaction with $\text{CH}_2=\text{CHCN}$. The yellow solution of 0.2 g of **1** in $\text{CH}_2=\text{CHCN}$ (0.5 mL) and H_2O (3 mL) turned colorless within 1 minute at 0 °C under N_2 . Addition of EtOH (10 mL) and Et_2O (10 mL) resulted in precipitation of pale yellow powders which were collected by filtration, washed with Et_2O (10 mL) and dried under vacuum. The yield was 0.17 g. ^1H NMR (D_2O , 25 °C) 0.25, 2.42, 4.35

(3×m, 1H, CH₂=CHCN), 7.2-8.2 (m, 24H, P-C₆H₄SO₃); IR (Nujol) ν_{max}/cm^{-1} , 2240w (C≡N), 2054s, 2006w, 1977w (C≡O), 1650br, 3400s, br. (H₂O).

Reaction with H₂. Yellow solution of **1** (0.1 g) in H₂O (1 mL) turned colorless under H₂ (1 atm) at 0 °C within 10 minutes. Addition of cold EtOH (5 mL) and Et₂O (10 mL) to the reaction mixture resulted in precipitation of beige powders which were collected by filtration, washed with Et₂O (10 mL) and dried under vacuum. The yield was 0.08 g. ¹H NMR (D₂O, 25 °C) δ -6.85 (t, Ir-H, $J_{\text{P-H}}=17.3$ Hz), 7.2-8.0 (m, P-C₆H₄-SO₃Na); IR (Nujol) ν_{max}/cm^{-1} 2098s, 2008m (C≡O), 1650br, 3400s, br. (H₂O).

Reaction with HC≡CH. A yellow solution of **1** (0.32 g) in H₂O (3 mL) turned pale yellow under HC≡CH (1 atm) within 10 minutes at 0 °C. Addition of cold EtOH (10 mL) and Et₂O (10 mL) to the reaction mixture resulted in precipitation of pale yellow powders which were collected by filtration, washed with Et₂O (10 mL) and dried under vacuum. The yield was 0.315 g. ¹H NMR (D₂O, 25 °C) δ 5.38, 5.87, 6.52, 7.40 (4×m, 1H, Ir-C₄H₄ moiety), 7.6-8.0 (m, 24H, P-C₆H₄SO₃Na); ¹³C NMR (D₂O, 25 °C) δ 129.0 (t, $J_{\text{P-C}}=6.3$ Hz, α -C of Ir-C₄H₄), 159.0 (t, $J_{\text{P-C}}=6.3$ Hz, α -C of Ir-C₄H₄), 130.1, 147.0 (2×s, β -C of Ir-C₄H₄), 178.2 (t, $J_{\text{P-C}}=7.6$ Hz, Ir-CO); ³¹P NMR (D₂O, 25 °C) δ 8.15; IR (Nujol) ν_{max}/cm^{-1} 2098s, 2008m (C≡O), 1650br, 3400s, br. (H₂O).

Catalytic Hydration of Alkynes. All the catalytic reactions were carried out practically in the same manner as described below. A 0.05 g of (ca. 3.3×10^{-5} mol) of IrCl(CO)(TPPTS)₂·xH₂O and an alkyne (1.0×10^{-4} mol) in aqueous solution (total volume=1 mL, see Table 1) were stirred for 24 hours at 25 °C under N₂, and organic compounds were extracted with CDCl₃ (1.5 mL) for product analysis performed by ¹H NMR spectral and GC/mass measurements. Acetylene hydration was carried out under the same experimental conditions under 1 atm of HC≡CH.

Acknowledgment. Authors wish to thank Sogang University, the Ministry of Education, Republic of Korea (Grant No. BSRI-95-3412) and the Korea Science and En-

gineering Foundation (Grant No. 94-0501-01-01-03) for their financial supports of this study.

References

- Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* **1994**, *33*, 200 and refs. therein.
- Gassner, F.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1465 and refs. therein.
- Bartik, T.; Bunn, B. B.; Bartik, B.; Hanson, B. E. *Inorg. Chem.* **1994**, *33*, 164 and refs. therein.
- Herrmann, W. A.; Kellner, J.; Riepl, H. *J. Organomet. Chem.* **1990**, *389*, 103.
- Saysell, D. M.; Borman, C. D.; Kwak, C.-H.; Sykes, A. G. *Inorg. Chem.* **1996**, *35*, 173.
- Larok, R. C. *Comprehensive Organic Transformations*; VCH, 1988, p 596-599.
- Hiscox, W.; Jennings, P. W. *Organometallics* **1990**, *9*, 1997 and refs. therein.
- Joo, F.; Toth, Z. *J. Mol. Catal.* **1980**, *8*, 369.
- Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485.
- Vaska, L.; Diluzio, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 2784.
- Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335.
- Chin, C. S.; Park, Y.; Kim, J.; Lee, B. *Chem. Commun.* **1995**, 1495.
- Chin, C. S.; Oh, M.; Lee, H. *Organometallics* **1997**, *16*, 816.
- For examples, see (a) Farnetti, E.; Kaspar, J.; Graziani, M. *J. Mol. Catal.* **1990**, *5*, 63. (b) Chin, C. S.; Shin, J. H.; Kim, J. B. *J. Organomet. Chem.* **1988**, *356*, 381.
- For enol detection, see (a) Chin, C. S.; Park, J. *Chem. Commun.* **1987**, 1214. (b) Chin, C. S.; Lee, S. Y.; Park, J.; Kim, S. *J. Am. Chem. Soc.* **1988**, *110*, 8244.
- Chin, C. H.; Chang, W.-T. Unpublished results.