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pH-Selective Synthesis and Structures of Alkynyl, Acyl, and Ketonyl Intermediates in Anti-Markovnikov and Markovnikov Hydrations of a Terminal Alkyne with a Water-Soluble Iridium Aqua Complex in Water

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Abstract: Chemoselective synthesis and isolation of alkynyl $[Cp^*Ir^{III}(bpy)CCPh]^+$ (**2**, $Cp^* = \eta^5$-C_5Me_5, bpy = 2,2′-bipyridine), acyl $[Cp^*Ir^{III}(bpy)C(O)CH_2Ph]^+$ (**3**), and ketonyl $[Cp^*Ir^{III}(bpy)CH_2C(O)Ph]^+$ (**4**) intermediates in anti-Markovnikov and Markovnikov hydration of phenylacetylene in water have been achieved by changing the pH of the solution of a water-soluble aqua complex $[Cp^*Ir^{III}(bpy)(H_2O)]^{2+}$ (**1**) used as the same starting complex. The alkynyl complex [**2**]$_2$·SO_4 was synthesized at pH 8 in the reaction of **1**·SO_4 with H_2O at 25 °C, and was isolated as a yellow powder of **2**·X (X = CF_3SO_3 or PF_6) by exchanging the counteranion at pH 8. The acyl complex [**3**]$_2$·SO_4 was synthesized by changing the pH of the aqueous solution of [**2**]$_2$·SO_4 from 8 to 1 at 25 °C, and was isolated as a red powder of **3**·PF_6 by exchanging the counteranion at pH 1. The hydration of phenylacetylene with **1**·SO_4 at pH 4 at 25 °C gave a mixture of [**2**]$_2$·SO_4 and [**4**]$_2$·SO_4. After the counteranion was exchanged from SO_4^{2-} to $CF_3SO_3^-$, the ketonyl complex **4**·CF_3SO_3 was separated from the mixture of **2**·CF_3SO_3 and **4**·CF_3SO_3 because of the difference in solubility at pH 4 in water. The structures of **2**−**4** were established by IR with ^{13}C-labeled phenylacetylene ($Ph^{12}C{\equiv}{}^{13}CH$), electrospray ionization mass spectrometry (ESI-MS), and NMR studies including ^{1}H, ^{13}C, distortionless enhancement by polarization transfer (DEPT), and correlation spectroscopy (COSY) experiments. The structures of **2**·PF_6 and **3**·PF_6 were unequivocally determined by X-ray analysis. Protonation of **3** and **4** gave an aldehyde (phenylacetaldehyde) and a ketone (acetophenone), respectively. Mechanism of the pH-selective anti-Markovnikov vs Markovnikov hydration has been discussed based on the effect of pH on the formation of **2**−**4**. The origins of the alkynyl, acyl, and ketonyl ligands of **2**−**4** were determined by isotopic labeling experiments with D_2O and $H_2{}^{18}O$.

Introduction

Organic synthesis catalyzed by transition metal complexes in water is rapidly developing because the use of water as a solvent, a reagent, and a ligand has many potential advantages such as alleviation of environmental problems associated with the use of organic solvents, simple isolation of organic products by phase separation, and reaction-specific pH selectivity.[1−7]

Since Tokunaga and Wakatsuki reported on the first anti-Markovnikov hydration of terminal alkynes into aldehydes

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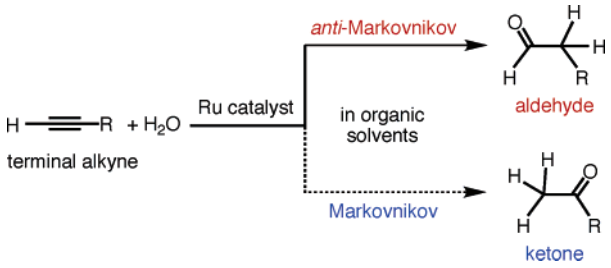
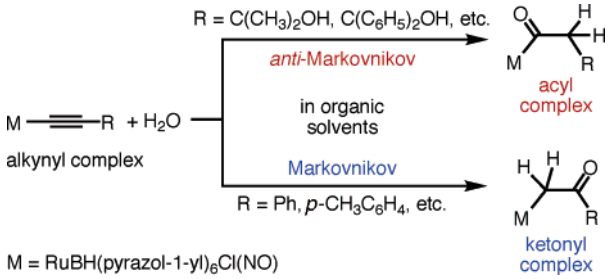
catalyzed by a ruthenium complex in organic solvents (vide infra),[8] a variety of transition metal complexes have been investigated as catalysts for the anti-Markovnikov hydration in organic solvents.[9−12]



Onishi and co-workers have shown the chemoselective isolation of acyl complexes (as an intermediate of anti-Markovnikov hydration) and ketonyl complexes (as an intermediate of Markovnikov hydration) in organic solvents by changing the substituent groups (R) in the hydrated alkynyl complexes as follows.[13]



Anti-Markovnikov hydration of terminal alkynes (such as propargylic alcohols) catalyzed by ruthenium complexes in aqueous media has recently been investigated.[14−16] However, chemoselective synthesis and isolation of the intermediates in the transition metal catalyzed anti-Markovnikov and Markovnikov hydration of terminal alkynes in water rather than in organic solvents have yet to be achieved.

We report herein the first example of pH-selective synthesis and isolation of an alkynyl intermediate $[Cp^*Ir^{III}(bpy)CCPh]^+$ (**2**, Cp* = η^5-C_5Me_5, bpy = 2,2′-bipyridine) and an acyl intermediate $[Cp^*Ir^{III}(bpy)C(O)CH_2Ph]^+$ (**3**) in the anti-Markovnikov hydration as well as a ketonyl intermediate $[Cp^*Ir^{III}(bpy)CH_2C(O)Ph]^+$ (**4**) in the Markovnikov hydration of a terminal alkyne (phenylacetylene) by using the same water-soluble aqua complex $[Cp^*Ir^{III}(bpy)(H_2O)]^{2+}$ (**1**) as a starting complex in water. The structures of **2**−**4** were established by IR with ^{13}C-labeled phenylacetylene ($Ph^{12}C{\equiv}{}^{13}CH$), electrospray ionization mass spectrometry (ESI-MS), and ^1H and ^{13}C NMR studies, which were assisted by the use of distortionless enhancement by polarization transfer (DEPT) and correlation spectroscopy (COSY) techniques. The structures of **2** and **3** were definitely determined by X-ray analysis. The isolation of **2**−**4** allowed us to investigate their reactivity toward H_2O.

Experimental Section

Materials and Methods. All experiments were carried out under an Ar atmosphere by using standard Schlenck techniques and a glovebox. The aqua complex $[Cp^*Ir^{III}(bpy)(H_2O)]SO_4$ (**1**·SO_4) was prepared by the method described in the literature.[17] All chemicals (highest purity available) were purchased from Aldrich Chemicals Co. and used without further purification. The manipulations in acidic media were carried out with plasticware and glassware (without metals). D_2O (99.9% D) and 40% NaOD/D_2O (99% D) were purchased from Cambridge Isotope Laboratories. $H_2{}^{18}O$ (96.5% ^{18}O), 65% DNO_3/D_2O (99% D), and ^{13}C-labeled phenylacetylene ($Ph^{12}C{\equiv}{}^{13}CH$, 99% ^{13}C) were purchased from Isotec Inc. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore; Milli-RO 5 plus and Milli-Q plus). The spectra of ^1H and ^{13}C NMR, DEPT-135, and H−H and C−H COSY were recorded on JEOL-JNM-AL300 and JEOL-JNM-ECP400 spectrometers at 25 °C. IR spectra of solid samples were recorded on a Thermo Nicolet NEXUS 870 FT-IR instrument using 2 cm^{-1} standard resolution at ambient temperature, and infrared spectra of aqueous solutions were obtained by an ASI ReactIR 1000 spectrophotometer under an Ar atmosphere. ESI-MS data were collected on an API 365 triple quadrupole mass spectrometer (PE-Sciex) in positive detection mode, equipped with an ion spray interface. The sprayer was held at a potential of +5.0 kV, and compressed N_2 was employed to assist liquid nebulization. The orifice potential was maintained at +20 V. A Nissin magnetic stirrer (Model SW-R800) was used.

pH Adjustment. In a pH range of 1−9, pH values of the solutions were determined by a pH meter (TOA, HM-18E) equipped with a pH combination electrode (TOA, GS-5015C). The pH of the solution was adjusted by using 1 M HNO_3/H_2O (pH 1−3), 0.1 M CH_3COOH/CH_3COONa (pH 4−6), and 0.2 M Na_2HPO_4/NaH_2PO_4 (pH 7−9) solutions. During the reaction, a stainless steel micro pH probe (IQ Scientific Instruments, Inc., PH15-SS) was dipped in the reaction mixture at 70 °C under an Ar atmosphere, and the pH of the solution was monitored by a pH meter (IQ Scientific Instruments, Inc., IQ200). It was confirmed that the pH of the solution does not change during the course of the reactions under the conditions of this study. To determine the exact pH values, the ^1H NMR experiments were performed by dissolving the samples in HNO_3/H_2O in an NMR tube (diameter = 5.0 mm) with a sealed capillary tube (diameter = 1.5 mm) containing 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP, 500 mM, as the reference with the methyl proton resonance set at 0.00 ppm) dissolved in D_2O (for deuterium lock). Values of pD were corrected by adding 0.4 to the observed values.[18]

$[Cp^*Ir^{III}(bpy)CCPh]X$ (2·X, Where X = CF_3SO_3 or PF_6). A reaction of $[Cp^*Ir^{III}(bpy)(OH_2)]SO_4$ (**1**·SO_4, 30 mg, 50 μmol) with phenylacetylene (25.5 mg, 250 μmol) in H_2O (30 mL) at pH 8 at 25 °C for 10 min provides a yellow solution of [**2**]$_2$·SO_4. To the solution was added CF_3SO_3Na (17.2 mg, 100 μmol) or NH_4PF_6 (16.3 mg, 100 μmol) at pH 8 in water (3 mL), and the mixture was stirred for 1 min

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to afford a yellow powder of **2**·CF_3SO_3 or **2**·PF_6, which was collected by filtration, washed with water, and dried in vacuo (yield of **2**·CF_3SO_3: 88% based on **1**·SO_4; yield of **2**·PF_6: 84% based on **1**·SO_4). ^{1}H NMR of **2**·CF_3SO_3 (300 MHz, in $CDCl_3$, reference to TMS, 25 °C): δ 1.80 (s, 15H), 6.97 (d, 2H), 7.04 (m, 3H), 7.65 (t, 2H), 8.20 (t, 2H), 8.69 (d, 2H), 8.75 (d, 2H). ^{13}C NMR of **2**·CF_3SO_3 (in $CDCl_3$, reference to TMS, 25 °C): δ 8.76 {s; η^5-$C_5(CH_3)_5$}, 87.33 {s; *C*≡C}, 91.63 {s; η^5-*C*$_5$(CH$_3$)$_5$}, 99.70 {s; C≡*C*}, 125.28 {s; *C*H of bpy}, 125.75 {s; *C*H of Ph}, 127.08 {s; *C*H of Ph}, 127.82 {s; *C*H of Ph}, 128.10 {s; *C*H of Ph}, 131.71 {s; *C*H of Ph}, 139.98 {s; *C*H of bpy}, 151.03 {s; *C*H of bpy}, 155.71 {s; *C*H of bpy}. Anal. Calcd for $C_{29}H_{28}N_2F_3Ir_1O_3S_1$ (**2**·CF_3SO_3): C, 47.47; H, 3.85; N, 3.82. Found: C, 47.18; H, 3.77; N, 3.81.

[Cp*Ir^{III}(bpy)C(O)CH$_2$Ph]PF$_6$ (3·PF$_6$). Method A: The alkynyl complex [**2**]$_2$·SO_4 was prepared by the reaction of **1**·SO_4 (30 mg, 50 μmol) with phenylacetylene (25.5 mg, 250 μmol) in H_2O (30 mL) at pH 8 at 25 °C for 10 min. The pH of the aqueous solution of [**2**]$_2$·SO_4 was changed from 8 to 1 at 25 °C. To the solution was added NH_4PF_6 (16.3 mg, 100 μmol) in H_2O (3 mL) to provide a red powder of **3**·PF_6, which was collected by filtration (yield: 78% based on **1**·SO_4).

Method B: Phenylacetylene (51.0 mg, 50 mmol) was added to 0.1 M HNO_3/H_2O solution (20 mL) of **1**·SO_4 (60 mg, 0.1 mmol). After the solution was stirred at 70 °C for 10 min, the color of the solution turned to red. To the solution was added NH_4PF_6 (16.3 mg, 0.1 mmol) in H_2O (3 mL) to form a red powder of **3**·PF_6 {yield: 86% based on **1**·SO_4}. ^{1}H NMR (300 MHz, in $CDCl_3$, reference to TMS, 25 °C): δ 1.64 (s, 15H), 3.44 (s, 2H), 6.43 (d, 2H), 6.93 (m, 3H), 7.72 (t, 2H), 8.07 (t, 2H), 8.23 (d, 2H), 8.88 (d, 2H). ^{13}C NMR (in $CDCl_3$, reference to TMS, 25 °C): δ 8.36 {s; η^5-$C_5(CH_3)_5$}, 63.53 {s; C(O)*C*H$_2$}, 92.64 {s; η^5-*C*$_5$(CH$_3$)$_5$}, 124.01 {s; *C*H of bpy}, 126.29 {s; *C*H of Ph}, 128.23 {s; *C*H of Ph}, 128.26 {s; *C*H of bpy}, 128.41 {s; *C*H of Ph}, 128.41 {s; *C*H of Ph}, 133.07 {s; *C*H of Ph}, 139.26 {s; *C*H of bpy}, 151.38 {s; *C*H of bpy}, 155.55 {s; *C*H of bpy}, 222.0.67 {s; *C*(O)CH$_2$}. Anal. Calcd for $C_{28}H_{30}N_2F_6Ir_1O_1P_1$·$0.5H_2O$: C, 44.44; H, 4.12; N, 3.70. Found: C, 44.44; H, 4.01.; N, 3.81.

[Cp*Ir^{III}(bpy)CH$_2$C(O)Ph]CF$_3$SO$_3$ (4·CF$_3$SO$_3$). The reaction of **1**·SO_4 (0.35 mmol) with phenylacetylene (1.75 mmol) in H_2O (30 mL) at pH 4 (0.1 M CH_3COOH/CH_3COONa buffer) at 25 °C for 10 min gave a mixture of [**2**]$_2$·SO_4 and [**4**]$_2$·SO_4. To the solution was added CF_3SO_3Na (3.5 mmol) in H_2O (3 mL) at pH 4 to give the powder of **2**·CF_3SO_3, which was removed by filtration. The solution was extracted with $CHCl_3$. Upon evaporation of $CHCl_3$, a brown powder was obtained. The powder was recrystallized from MeOH/diethyl ether to provide a very hygroscopic brown powder of **4**·CF_3SO_3 (yield: 29% based on **1**·SO_4). ^{1}H NMR (300 MHz, in $CDCl_3$, reference to TMS, 25 °C): δ 1.66 (s, 15H), 3.06 (s, 2H), 7.00 (m, 5H), 7.43 (t, 2H), 7.97 (t, 2H), 8.30 (d, 2H), 8.40 (d, 2H). ^{13}C NMR (in $CDCl_3$, reference to TMS, 25 °C): δ 8.20 {s; η^5-$C_5(CH_3)_5$}, 15.0.75 {s; *C*H$_2$C(O)}, 90.18 {s; η^5-*C*$_5$(CH$_3$)$_5$}, 124.41 {s; *C*H of bpy}, 126.50 {s; *C*H of Ph}, 127.73 {s; *C*H of bpy}, 128.02 {s; *C*H of Ph}, 131.74 {s; *C*H of Ph}, 138.80 {s; *C*H of bpy}, 139.05 {s; *C* of Ph}, 150.64 {s; *C*H of bpy}, 154.98 {s; *C* of bpy}, 202.06 {s; *C*(O)CH$_2$}. The ketonyl complex **4**·CF_3SO_3 is very hygroscopic.

Typical Procedure for the Hydration of Phenylacetylene with the Aqua Complex 1. The pH of the solution of **1**·SO_4 (2.4 mg, 3.93 mmol) in H_2O (0.5 mL) was adjusted by using HNO_3/H_2O, CH_3COOH/CH_3COONa, Na_2HPO_4/NaH_2PO_4, and $NaHCO_3$/NaOH. Ten equivalents of phenylacetylene (4.0 mg, 39.3 mmol) was added to the solution. The mixture was vigorously stirred (1000 rpm, Nissin magnetic stirrer Model SW-R700) for 10 min at 70 °C. After it was cooled to 0 °C, a counteranion salt was added to the resulting mixture. It was extracted by $CDCl_3$. The ratio of complexes **1**−**4** in the $CDCl_3$ solution has been determined by ^{1}H NMR. It was confirmed that no reaction occurred in the absence of complexes **1** (as blank experiments).

X-ray Crystallographic Analysis. Crystallographic data for **2**·PF_6 and **3**·PF_6 have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-237677 and 237678, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK {fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk}. Measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). Data were collected and processed using the CrystalClear program (Rigaku). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

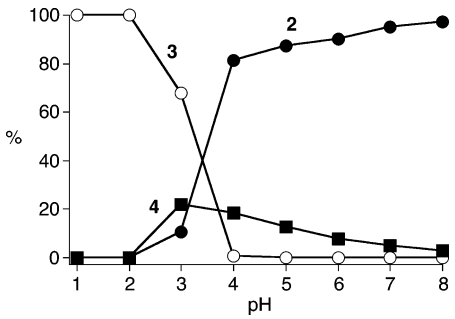

Figure 1. pH-dependent formation ratio of **2**−**4** on the reaction of **1** with phenylacetylene in H_2O at 70 °C after 10 min.

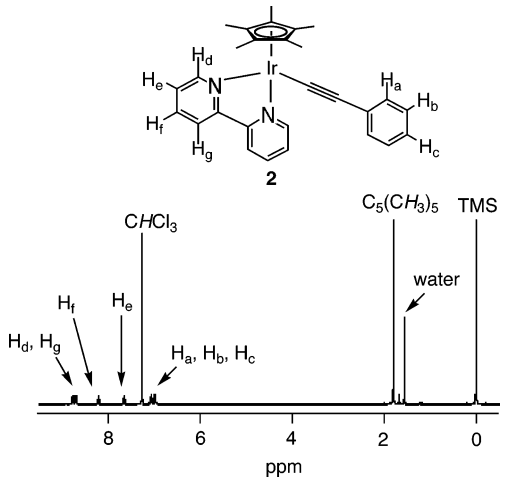

Figure 2. ^{1}H NMR spectrum of **2**·CF_3SO_3 in $CDCl_3$ at 25 °C. TMS, reference with the methyl proton resonance set at 0.00 ppm.

Results and Discussion

pH-Selective Synthesis and Structure of the Alkynyl Complex 2. The water-soluble aqua complex **1**·SO_4 reacts with phenylacetylene in H_2O at 25 °C for 10 min to give the water-soluble alkynyl complex [**2**]$_2$·SO_4. The formation of [**2**]$_2$·SO_4 is pH-dependent as shown in Figure 1 (filled circles). The alkynyl complex **2** was isolated as a yellow powder of **2**·CF_3SO_3 by addition of CF_3SO_3Na to the solution of [**2**]$_2$·SO_4 at pH 8 at 25 °C. The structure of **2**·CF_3SO_3 was established by NMR (^{1}H and ^{13}C NMR, DEPT-135, and H−H and C−H COSY), IR, and ESI-MS. Figure 2 shows ^{1}H NMR spectrum of **2**·CF_3SO_3 in $CDCl_3$. The signal at 1.80 ppm corresponds to the Cp* protons {$C_5(CH_3)_5$} of **2**·CF_3SO_3. ^{13}C NMR (S1), DEPT-135 (S2), H−H COSY (S3), and C−H COSY (S4) spectra of **2**·CF_3SO_3 are shown in the Supporting Information. In an IR spectrum in the 1400−2600 cm^{-1} region as a KBr disk of **2**·CF_3SO_3 (Figure 3a), a prominent peak at 2114 cm^{-1} was assigned to ν(C≡C) that shifts to 2081 cm^{-1} by isotopic substitution of a carbon atom in the alkynyl ligand (Ir−^{13}C≡^{12}CPh, Figure 3b). The shift value (33 cm^{-1}) agrees well with

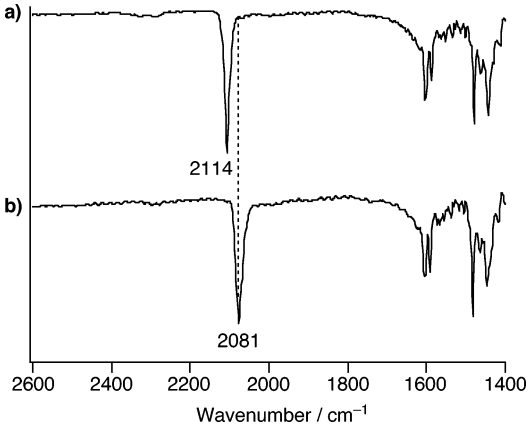

Figure 3. (a) IR spectrum of **2**·CF_3SO_3 as a KBr disk. (b) IR spectrum of ^{13}C-labeled **2**·CF_3SO_3 {[Cp*Ir^{III}(bpy)(^{13}CCPh)](CF_3SO_3)} as a KBr disk.

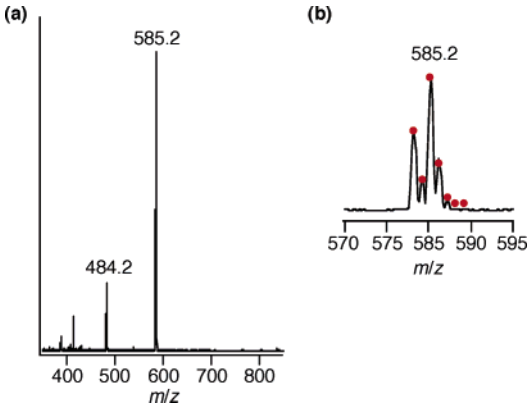

Figure 4. (a) Positive-ion ESI mass spectrum of **2**·CF_3SO_3 in H_2O. (b) Signal at *m*/*z* 585.2 for [**2**]$^+$. Red circles, calculated isotopic distribution for [**2**]$^+$.

that expected by Hooke's law calculation for a pure C≡C stretching mode. A positive-ion ESI mass spectrum of **2**·CF_3SO_3 in H_2O is shown in Figure 4a. The prominent signal at *m*/*z* 585.2 {relative intensity (*I*) = 100% in the range of *m*/*z* 400−800} has a characteristic distribution of isotopomers (Figure 4b) that matches well with the calculated isotopic distribution (red circles) for [**2**]$^+$.

pH-Selective Synthesis and Structure of the Acyl Complex 3. The water-soluble acyl complex [**3**]$_2$·SO_4 was synthesized by changing the pH of the solution of the alkynyl complex [**2**]$_2$·SO_4 in H_2O from 8 to 1 at 25 °C as shown in Figure 1 (open circle). The acyl complex **3** was isolated as a red powder of **3**·PF_6 by addition of NH_4PF_6 to the solution of [**3**]$_2$·SO_4 at pH 1. The structure of **3**·PF_6 was determined by NMR (^{1}H and ^{13}C NMR, DEPT-135, and H−H and C−H COSY), IR, and ESI-MS. Figure 5 shows the ^{1}H NMR spectrum of **3**·PF_6 in $CDCl_3$. The signal of the Cp* protons of **3** was observed at 1.64 ppm. ^{13}C NMR (S5), DEPT-135 (S6), H−H COSY (S7), and C−H COSY (S8) spectra of **3**·PF_6 are shown in the Supporting Information. Figure 6a shows an IR spectrum in the 1400−1800 cm^{-1} region as a KBr disk of **3**·PF_6. The peaks at 1632 and 1644 cm^{-1} shifted to 1593 and 1605 cm^{-1} by isotopic substitution of ^{12}C for ^{13}C in the C═O group (Figure 6b). A positive-ion ESI mass spectrum of [**3**]$_2$·SO_4 in H_2O shows a prominent signal at *m*/*z* 603.2 (*I* = 100% in the range of *m*/*z* 400−800, Figure 7a), which has a characteristic distribution of isotopomers (Figure 7b) that matches well with the calculated isotopic distribution (red circles) for [**3**]$^+$.

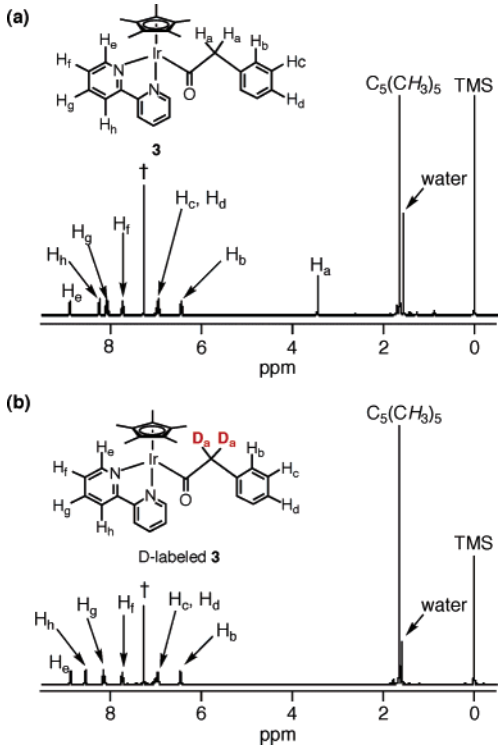

Figure 5. ^{1}H NMR spectrum of **3**·PF_6 (a) and D-labeled **3**·PF_6 (b) in $CDCl_3$ at 25 °C. TMS, reference with the methyl proton resonance set at 0.00 ppm; †, $CHCl_3$.

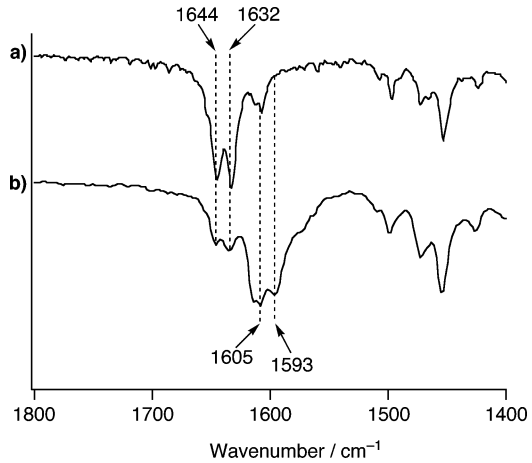

Figure 6. (a) IR spectrum of **3**·PF_6 as a KBr disk. (b) IR spectrum of ^{13}C-labeled **3**·PF_6 {[Cp*Ir^{III}(bpy)(^{13}C(O)CH_2Ph)](CF_3SO_3)} as a KBr disk.

It is known that acyl complexes can arrive from vinylidene species.[19] It has also been proposed that anti-Markovnikov hydration of alkynes proceeds through vinylidene intermediates.[20−25] However, such vinylidene species were not observed in our hydration system with the Ir complexes in water.

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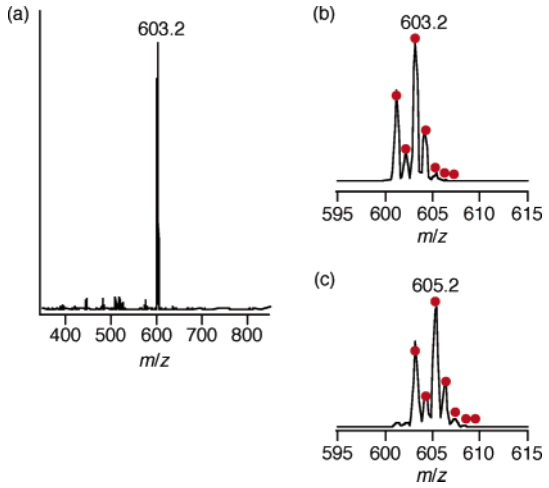

Figure 7. (a) Positive-ion ESI mass spectrum of $[\mathbf{3}]_2 \cdot SO_4$ in H_2O. (b) The signal at *m*/*z* 603.2 corresponds to **3**. Red circles, calculated isotopic distribution for $[\mathbf{3}]^+$. (c) Positive-ion ESI-MS spectrum of ^{18}O-labeled **3**. Red circles, calculated isotopic distribution for [^{18}O-labeled $\mathbf{3}]^+$.

pH-Selective Synthesis and Structure of the Ketonyl Complex 4. The reaction of $\mathbf{1} \cdot SO_4$ with phenylacetylene in H_2O at pH 4 at 25 °C for 10 min gave a mixture of $[\mathbf{2}]_2 \cdot SO_4$ and $[\mathbf{4}]_2 \cdot SO_4$ as shown in Figure 1 (filled squares). To the solution was added CF_3SO_3Na in H_2O at pH 4 to give the powder of $\mathbf{2} \cdot CF_3SO_3$, which was removed by filtration. The solution was extracted with $CHCl_3$. Upon evaporation of $CHCl_3$, a brown powder was obtained. After recrystallization (MeOH/diethyl ether), we isolated a very hygroscopic brown powder of $\mathbf{4} \cdot CF_3SO_3$. The structure of $\mathbf{4} \cdot CF_3SO_3$ was determined by NMR (^1H and ^{13}C NMR, DEPT-135, and H−H and C−H COSY), IR, and ESI-MS. Figure 8 shows the ^1H NMR spectrum of $\mathbf{4} \cdot CF_3SO_3$ in $CDCl_3$. The signal at 1.66 ppm corresponds to the Cp* protons of $\mathbf{4} \cdot CF_3SO_3$. ^{13}C NMR (S9), DEPT-135 (S10), H−H COSY (S11), and C−H COSY (S12) spectra of $\mathbf{4} \cdot CF_3SO_3$ are shown in the Supporting Information. Figure 9 shows an IR spectrum in the 1200−2000 cm^{-1} region as a KBr disk of $\mathbf{4} \cdot CF_3SO_3$. A positive-ion ESI mass spectrum of $\mathbf{4} \cdot CF_3SO_3$ in CH_3Cl shows a prominent signal at *m*/*z* 603.2 (I = 100% in the range of *m*/*z* 400−800, Figure S13), which coincides with the signal observed in the ESI mass spectrum of the acyl complex $[\mathbf{3}]^+$ as shown in Figure 7a.

Crystal Structure of the Alkynyl Complex 2. Yellow crystals of $\mathbf{2} \cdot PF_6$ used for the X-ray analysis were obtained from MeOH/diethyl ether. Crystal data, data collection parameters, and structure refinement for $\mathbf{2} \cdot PF_6$ are listed in Table 1. Selected bond lengths and angles for $\mathbf{2} \cdot PF_6$ are listed in Table 2. An ORTEP drawing of **2** is shown in Figure 10. Complex **2** adopts a distorted octahedral coordination that is surrounded by one Cp*, one bpy, and one alkynyl ligand. The Ir1−C1 bond length of **2** is 2.006(9) Å, which is very close to the metal−C bond length observed in $[Cp^*Ru(CCH)(PEt_3)_2H]BPh_4$ {2.034(4) Å},[25a] $[Ru(CCH)(cym)(phen)]BAr'_4$ (cym = η^6-4-methylisopropylbenzene, phen = 1,10-phenanthroline, Ar′ = 3,5-bis-(trifluoromethyl)phenyl) {2.022(9) Å},[26] and [Cp*Ir(CCCMe$_3$)(Pro)(phen)] (Pro = L-prolinate) {2.012(8) Å}[27] within the error limits. The C1−C2 bond length of **1** is 1.21(1) Å, which is

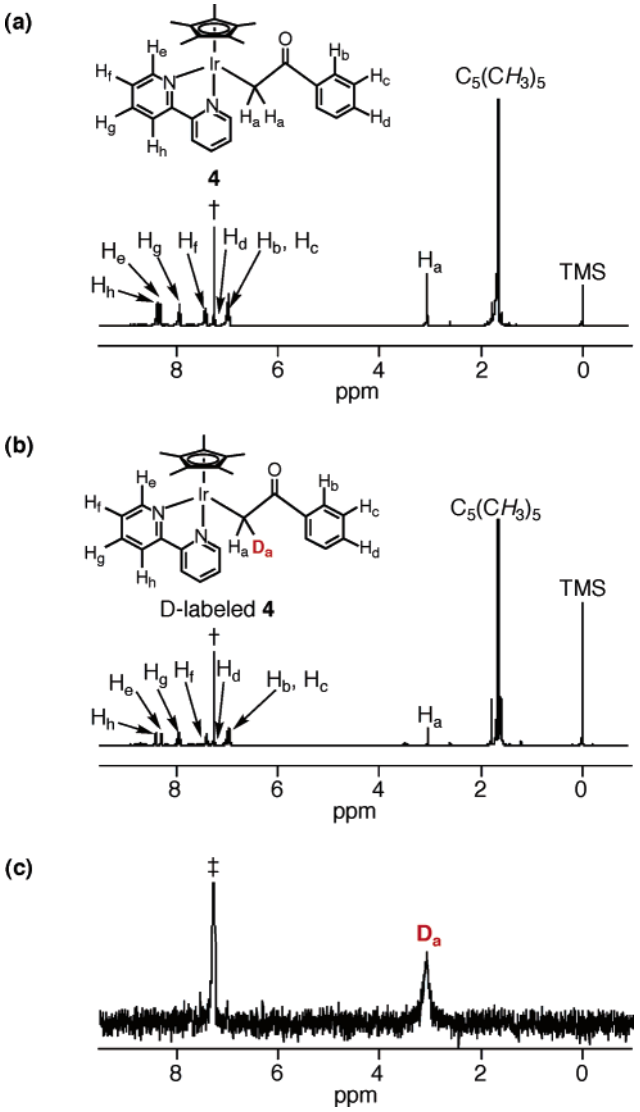

Figure 8. (a) ^1H NMR spectrum of $\mathbf{4} \cdot CF_3SO_3$ in $CDCl_3$ at 25 °C. TMS, reference with the methyl proton resonance set at 0.00 ppm; †, $CHCl_3$. (b) ^1H NMR spectrum of D-labeled $\mathbf{4} \cdot CF_3SO_3$ in $CDCl_3$ at 25 °C. (c) ^2H NMR spectrum of D-labeled $\mathbf{4} \cdot CF_3SO_3$ in $CHCl_3$. ‡, $CDCl_3$

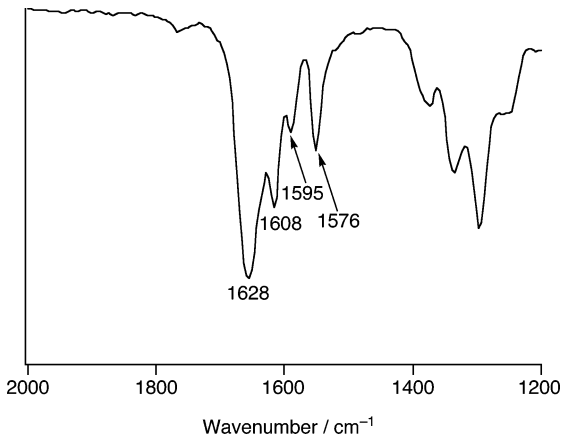

Figure 9. IR spectrum of $\mathbf{4} \cdot CF_3SO_3$ as a KBr disk.

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Table 1. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for {[Cp*Ir^{III}(bpy)CCPh](PF$_6$)} **2**·PF$_6$ and {[Cp*Ir^{III}(bpy)C(O)CH$_2$Ph](PF$_6$)} **3**·PF$_6$

compound	**2**·PF$_6$	**3**·PF$_6$
empirical formula	$C_{28}H_{28}F_6IrN_2P$	$C_{28}H_{30}F_6IrN_2OP$
fw	729.73	747.74
cryst color	yellow	orange
cryst dimen (mm)	0.20 × 0.12 × 0.12	0.20 × 0.18 × 0.15
cryst syst	monoclinic	monoclinic
a (Å)	13.158(1)	14.873(5)
b (Å)	13.577(1)	12.882(4)
c (Å)	16.160(2)	29.567(10)
β (deg)	88.936(6)	95.768(4)
V (Å^3)	2886.2(5)	5635(3)
space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)
Z	4	8
D_{calc} (g cm^{-3})	1.679	1.762
F_{000}	1424	2928
μ(Mo Kα) (cm^{-1})	4.752	4.872
radiation (λ, Å)	0.7107	0.7107
temp (°C)	−50.0	−100.0
$2\theta_{max}$ (deg)	55	55
abs corr method	numerical	numerical
no. of reflns obsd (all, 2θ < 54.97°)	6586	12891
no. of params	343	703
R[a]	0.107	0.076
R_w[b]	0.155	0.098
R1[c]	0.056	0.045
goodness of fit indicator, S[d]	1.04	0.92
max shift/error in final cycle	0.004	0.002
max peak in final diff map (e Å^{-3})	4.52	5.36
min peak in final diff map (e Å^{-3})	−3.69	−3.41

[a] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $R1 = \sum||F_o^2| - |F_c||/\sum|F_o|$ for $I > 2.0\sigma(I)$ data. [d] Goodness of fit indicator, $S = [Sw(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables).

Table 2. Selected Bond Lengths (//Å) and Angles (ϕ/deg) for **2**·PF$_6$

Ir1−C1	2.006(9)	Ir1−N1	2.089(8)
Ir1−N2	2.095(8)	C1−C2	1.21(1)
C2−C3	1.49(1)	Ir1−C19	2.22(1)
Ir1−C20	2.19(1)	Ir1−C21	2.15(1)
Ir1−C22	2.17(1)	Ir1−C23	2.19(1)
C19−C20	1.44(2)	C19−C23	1.42(1)
C20−C21	1.40(2)	C21−C22	1.41(1)
C22−C23	1.40(1)		
Ir1−C1−C2	174.3(9)	C1−C2−C3	178(1)
C1−Ir1−N1	91.3(3)	C1−Ir1−N2	87.6(4)
N1−Ir1−N2	76.4(3)	C19−Ir1−C20	38.1(4)
C19−Ir1−C23	37.7(4)	C20−Ir1−C21	37.6(4)
C21−Ir1−C22	38.1(4)	C22−Ir1−C23	37.4(4)

close to a carbon−carbon triple bond {1.20(2) Å} of an alkynyl complex which was determined previously by X-ray analysis.[28]

Crystal Structure of the Acyl Complex 3. Orange crystals of **3**·PF$_6$ obtained from $CHCl_3$/diethyl ether were used for the X-ray analysis. Crystal data, data collection parameters, and structure refinement for **3**·PF$_6$ are listed in Table 1. Selected bond lengths and angles for **3**·PF$_6$ are listed in Table 3. As depicted in Figure 11, complex **3** adopts a distorted octahedral coordination that is surrounded by one Cp*, one bidentate bpy, and one acyl ligand. The Ir1−C1 bond length of **3** is 2.037(8) Å, which is very close to the Ru−C bond length observed in [Ru(C(O)CH$_3$)(cym)(phen)]BAr′$_4$ {2.08(1) Å}.[26] The distances between the Ir atom and carbons of the Cp* ring of complex **3**

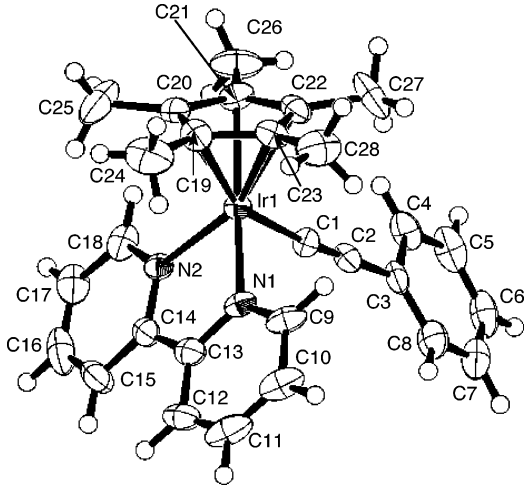

Figure 10. ORTEP drawing of **2**. The counteranion (PF$_6$) is omitted for clarity.

Table 3. Selected Bond Lengths (//Å) and Angles (ϕ/deg) for **3**·PF$_6$

Ir1−C1	2.037(8)	Ir1−N1	2.067(6)
Ir1−N2	2.080(5)	C1−C2	1.54(1)
C1−O1	1.229(9)	C2−C3	1.52(1)
Ir1−C19	2.253(7)	Ir1−C20	2.259(7)
Ir1−C21	2.179(7)	Ir1−C22	2.192(7)
Ir1−C23	2.171(7)	C19−C20	1.38(1)
C19−C23	1.45(1)	C20−C21	1.43(1)
C21−C22	1.43(1)	C22−C23	1.44(1)
Ir1−C1−C2	123.4(6)	Ir1−C1−O1	119.6(6)
C1−C2−C3	111.3(6)	C1−Ir1−N1	91.9(3)
C1−Ir1−N2	82.6(2)	N1−Ir1−N2	77.4(2)
C19−Ir1−C20	35.6(3)	C19−Ir1−C23	38.3(3)
C20−Ir1−C21	37.5(3)	C21−Ir1−C22	38.3(2)
C22−Ir1−C23	38.5(2)		

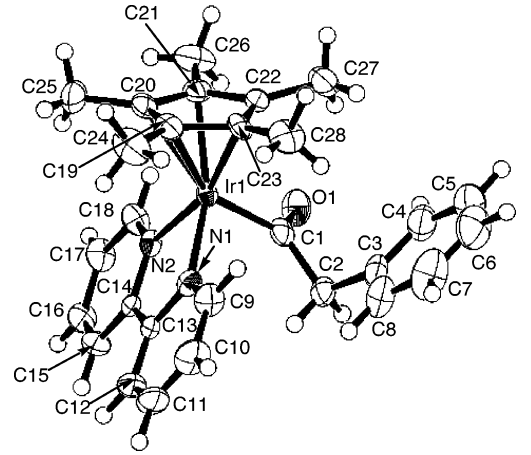

Figure 11. ORTEP drawing of **3**. The counteranion (PF$_6$) is omitted for clarity.

in the solid state are not equivalent; the distances of Ir1−C19 and Ir1−C20 {2.253(7) and 2.259(7) Å, respectively} trans to the acyl ligand are longer than those of Ir1−C21, Ir1−C22, and Ir1−C23 {2.179(7), 2.192(7), and 2.171(7) Å, respectively} trans to the bpy ligand. This indicates that the acyl ligand has a greater trans influence than the bpy ligand.

Reactivity of the Isolated Acyl Complex 3 and Ketonyl Complex 4 in Acidic Media. Although the isolated acyl complex **3**·PF$_6$ was acid-stable above pH 0 (1 M HNO_3/H_2O), it drastically reacted with 4 M HNO_3/H_2O (pH −0.6, 2.0 mL)

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(28) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79−154.

Table 4. Yield of Phenylacetaldehyde (**A**) and Acetophenone (**K**)[a]

	0 equiv phenylacetylene (noncatalytic reaction with **3** or **4**)				100 equiv phenylacetylene (catalytic reaction with **1**)			
	pH –0. 6		pH 1		pH –0. 6		pH 1	
aqua complex **1**					A K	TON: 0.1 TON: 2	A K	TON: 0 TON: 3
acyl complex **3**	A K	yield: 28% yield: 0%	A K	yield: 0% yield: 0%				
ketonyl complex **4**	A K	yield: 0% yield: 100%	A K	yield: 0% yield: 100%				

[a] The reactions were carried out at 70 °C for 10 min.

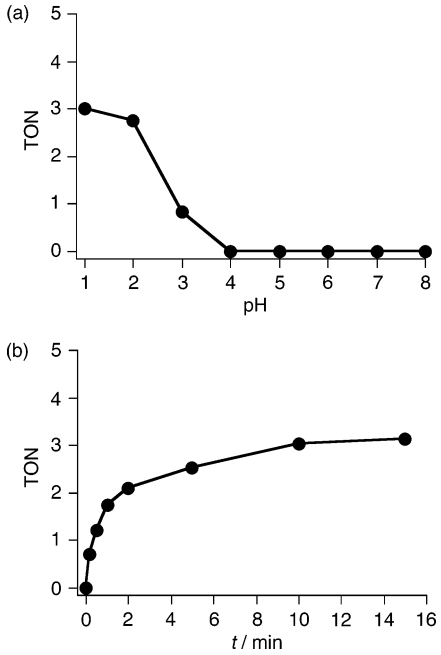
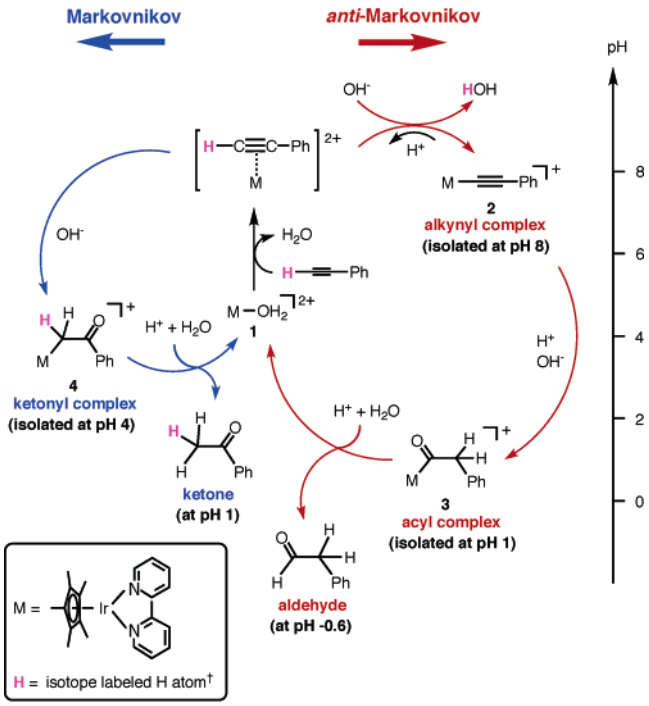


Figure 12. (a) pH-dependent TON for formation of acetophenone from reaction of **1**·SO_4 (2.62 μmol) with phenylacetylene (262 μmol) in water (1 mL) at 70 °C for 10 min. (b) Time course of the TONs of the hydration of phenylacetylene from the reaction of **1**·SO_4 (2.62 μmol) with phenylacetylene (262 μmol) in water (1 mL) at pH 1 at 70 °C.

Scheme 1



† The isotopic labeling experiments were carried out at 0 °C to avoids the back-reaction of **2** with protons.

at 70 °C for 10 min to yield phenylacetaldehyde (**A** in Table 4, yield: 28% based on **3**·PF_6), accompanied by regeneration of **1**. The formation of **1** was confirmed by ^{1}H NMR. The isolated ketonyl complex **4**·CF_3SO_3 quantitatively reacted with H_2O at pH 1.0 in H_2O at 70 °C for 10 min to provide acetophenone (**K** in Table 4, yield: 100% based on **4**·CF_3SO_3). It was confirmed that no isomerization of the acyl complex **3** into the ketonyl complex **4** occurred at pH 1 or pH −0.6.

Catalytic Anti-Markovnikov and Markovnikov Hydrations of Phenylacetylene with the Aqua Complex 1 in Acidic Media. Under catalytic conditions, the aqua complex **1** reacted with phenylacetylene (100 equiv) at pH 1 or pH −0.6 in H_2O at 70 °C for 10 min to give phenylacetaldehyde (anti-Markovnikov) and acetophenone (Markovnikov), as shown in Table 4. The turnover numbers (TON = the number of moles of acetophenone formed per mole of **1**) of the catalytic reaction of **1**·SO_4 with 100 equiv of phenylacetylene at pH 1 in H_2O at 70 °C for 10 min is pH-dependent, as shown in Figure 12a. The rate of hydration shows a maximum around pH 1. Figure 12b illustrates the time course of the hydration of phenylacetylene with **1**·SO_4 at pH 1 at 70 °C. The isolated ketonyl complex **4**·CF_3SO_3 quantitatively reacted with H_2O at pH 1.0 in H_2O at 70 °C for 10 min to provide acetophenone (yield: 100% based on **4**·CF_3SO_3). It was confirmed that no reaction occurred in the absence of complex **1** or **4** (as blank experiments).

Isotopic Labeling Experiments. To establish the origin of the acyl ligand in **3**, the reaction of **1**·SO_4 with phenylacetylene was carried out at pD 1.4 in D_2O at 70 °C. The results of ^{1}H NMR showed that the signal (observed at 3.44 ppm in Figure 5a) of the methylene protons of **3**·PF_6 was disappeared in the ^{1}H NMR spectrum (Figure 5b); i.e., the D atoms derived from D_2O were incorporated into the acyl ligand of **3**·PF_6. The reaction of **1**·SO_4 with phenylacetylene was also carried out at pH 1 in $H_2{}^{18}O$ at 70 °C. The results of ESI-MS (Figure 7c) showed that the ^{18}O atom from $H_2{}^{18}O$ was incorporated into the acyl ligand of **3**·SO_4.

Deuterium-labeled **4** was prepared by a reaction of **1**·SO_4 with phenylacetylene in D_2O at pD 4.4 at 0 °C for 10 min.[29] The results of ^{1}H NMR indicate that one of the methyl protons of the ketonyl ligand is derived from the terminal proton of phenylacetylene without H/D exchange at 25 °C (Figure 8b). The results of ^{2}H NMR show that the signal derived from the

(29) The isotopic labeling experiments were carried out at 0 °C to avoid the back-reaction of **2** with protons.

D-labeled methylene protons of **4**·CF_3SO_3 is observed at 3.06 ppm (Figure 8c).

ESI-MS, ^{1}H NMR, and GC-MS experiments using D_2O or $H_2{}^{18}O$ indicate that two of the methyl protons and one oxygen atom of acetophenone are derived from D_2O or $H_2{}^{18}O$, respectively.

Mechanism of the pH-Selective anti-Markovnikov vs Markovnikov Hydration. As shown in Figure 1, the formation of **2**−**4** from the reaction of **1**·SO_4 with phenylacetylene in H_2O at 70 °C for 10 min is pH-dependent. Scheme 1 summarizes the effect of pH on the formation of **2**−**4**. First, the reaction of the aqua complex **1** with phenylacetylene may produce a [M-phenylacetylene]$^{2+}$ species (M = Cp*Ir^{III}bpy) such as a π-complex (Scheme 1). Deprotonation of the [M-phenylacetylene]$^{2+}$ species occurs efficiently to give the alkynyl complex **2** around pH 8 (right-hand cycle in Scheme 1), in competition with nucleophilic attack of OH^- to the [M-phenylacetylene]$^{2+}$ species to form the ketonyl complex **4** in a pH range of about 2−6 (left-hand cycle). Isotopic labeling experiments at 25 °C (vide supra) clearly indicate that the ketonyl ligand of **4** is derived from the terminal proton of phenylacetylene. At pH 1−2, the protonation of **2** may occur, followed by nucleophilic attack of OH^-, leading to the formation of the acyl complex **3** (right-hand cycle). The protonation of **3** and **4** gives phenylacetaldehyde (anti-Markovnikov hydration) and acetophenone (Markovnikov hydration), respectively. Since the regioselectivity (anti-Markovnikov vs Markovnikov) results from only the change in pH, the regioselectivity originates from different attacking species (H^+ or OH^-) depending on pH as shown in Scheme 1.

In conclusion, we have succeeded in pH-selective isolation of an alkynyl intermediate [Cp*Ir^{III}(bpy)CCPh]$^+$ (**2**) and an acyl intermediate [Cp*Ir^{III}(bpy)C(O)CH_2Ph]$^+$ (**3**) in the anti-Markovnikov hydration as well as a ketonyl intermediate [Cp*Ir^{III}(bpy)CH_2C(O)Ph]$^+$ (**4**) in the Markovnikov hydration of a terminal alkyne (phenylacetylene) by starting from the same water-soluble aqua complex [Cp*Ir^{III}(bpy)(H_2O)]$^{2+}$ (**1**). The present study has provided valuable insight into the regioselective and catalytic hydration of a terminal alkyne.

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Supporting Information Available: Figures S1−S13, showing spectra for **2**−**4**, and crystallographic data (CIF) for **2**·PF_6 and **3**·PF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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