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# Acid-Promoted $sp^3$ C–H Bond Cleavage in a Series of (2-Allylphenoxo)ruthenium(II) Complexes. Mechanistic Insight into the Aryloxo–Acid Interaction and Bond Cleavage Reaction

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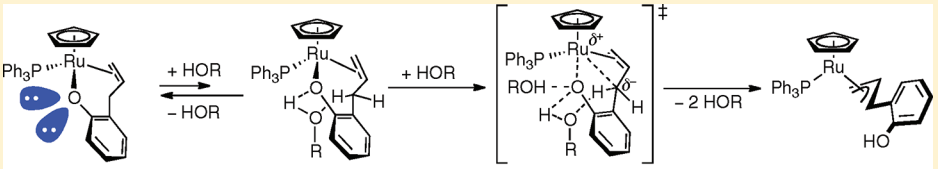
Supporting Information

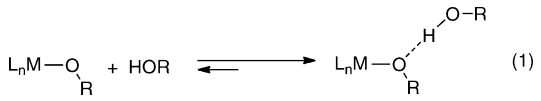



Acid-Promoted $sp^3$ C-H Bond Cleavage Reaction

**ABSTRACT:** A series of RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)(R)]$(PPh_3)_n$ complexes ($n$ = 2, R = H (**1a**); $n$ = 1, R = 4-OMe (**2b**), 4-Me (**2c**), 4-Ph (**2d**), 4-Br (**2e**), 4-$NO_2$ (**2f**), 6-OMe (**2g**), 6-Me (**2h**), 6-Ph (**2i**)) have been prepared in 27–76% yields. These 2-allylaryloxo complexes **1a** and **2b–f** are in equilibrium between RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)(R)-$\kappa^1O$]$(PPh_3)_2$ (**1**) and RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)(R)-$\kappa^1O,\eta^2C,C'$]$(PPh_3)$ (**2**) in solution, and **2g–i** do not react with $PPh_3$. The equilibrium constant $K_1$ ($K_1$ = [**2**][$PPh_3$]/[**1**]) is about the same for **1a** and **2b–f** ($K_1$ = 0.07–0.31 M). In contrast to the conventional aryloxo complexes of the late transition metals, treatment of **1a** and **2a–g** with weak Brønsted acids (HOR) gives a rapid equilibrium with **2**·HOR. The association constant $K_2$ ($K_2$ = [**2**·HOR]/([**2**][HOR])) increases on decreasing the p$K_a$ value of the acid employed and on increasing the induction effect of substituents at the 4-position in the aryloxo group. These features suggest present association being regarded as a simple acid–base interaction. Interestingly, further association of **2**·HOR with the second acid leads to the cleavage of the benzylic C–H bond, giving RuCp[$C_3H_4${1-$C_6H_3$(OH-2)(R)}-$\eta^3C,C',C''$]$(PPh_3)$ (**3**). The thermodynamic and kinetic studies suggest formation of hydrogen bonds among two Brønsted acid molecules, lone-pair electrons in the aryloxo oxygen, and a benzylic methylene proton. Such association makes the Ru(II) center more electrophilic to attack the benzylic carbon to give **3**.

## INTRODUCTION

Alkoxo and aryloxo complexes of low-valent late-transition-metal compounds are known to have highly basic properties, because the relatively electronegative metal center cannot accept most of the oxygen lone pair electrons.[1,2] There are numerous examples of hydrogen bonding between the alkoxo and aryloxo complexes of late transition metals and external alcohols or phenols, as shown in eq 1.[3]

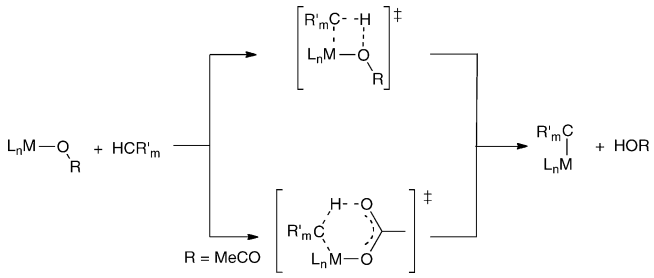



(1)

In the past decade, the alkoxo and aryloxo and also hydroxo and acetato ligands in late-transition-metal compounds have been revealed to accept a hydrogen of the less reactive C–H bond in benzene, arene, and methane by an electrophilic substitution mechanism (Scheme 1).[4]

We previously reported a series of internal $sp^3$ C–H bond cleavage reactions in alkoxo-,[5] aryloxo-,[6] and (arenethiolato)-ruthenium(II)[7] and (arenethiolato)platinum(II)[8] compounds. In these studies, we found that an acid-promoted $sp^3$ C–H bond cleavage reaction of the (2-allylphenoxo)ruthenium(II) complex RuCp[$OC_6H_4(CH_2CH{=}CH_2$-2)-$\kappa^1O$]$(PPh_3)_2$ (**1a**) gave the $\eta^3$-allylic complex RuCp[$C_3H_4${1-$C_6H_4$(OH-2)}-$\eta^3C,C',C''$]$(PPh_3)$ (**3a**) (Scheme 2).[9]

**Scheme 1**

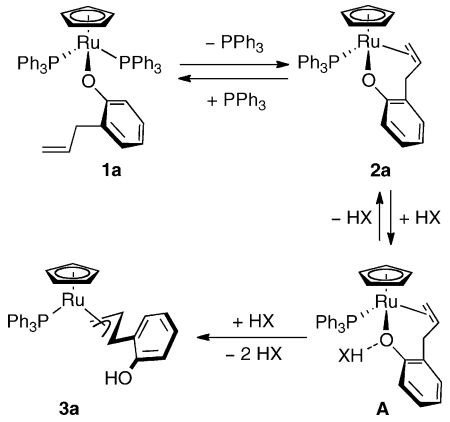



The preliminary results revealed the one-to-one association between the (2-allylphenoxo)ruthenium(II) complex **2a** and an acid, which was tentatively depicted as intermediate **A** in

**Received:** October 13, 2011
**Published:** December 20, 2011

**Scheme 2**

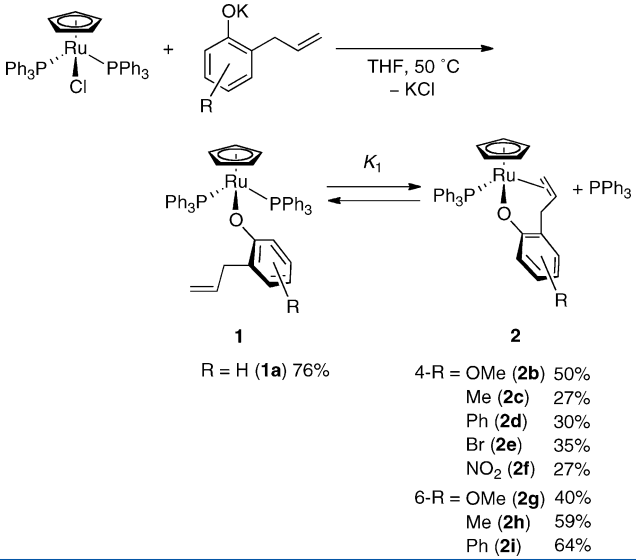



Scheme 2, to which the second acid association was necessary to cleave the $sp^3$ C–H bond of a benzylic methylene proton to give **3a**. It is worthwhile to note that the added Brønsted acid does not lead to the simple protonolysis of the aryloxo group[10] but promotes the internal $sp^3$ C–H bond cleavage reaction. Such a process was unprecedented to the best of our knowledge. This reaction cannot be explained by the mechanisms shown in eq 1 or Scheme 1, and the question arises as to how the Brønsted acid cleaves the inactive $sp^3$ C–H bond. This question prompted us to undertake further mechanistic investigations. We disclose here a full account of this new reaction with extensive results involving a mechanistic insight into the origin of the aryloxo–acid interaction and bond cleavage reaction.

## RESULTS AND DISCUSSION

**1. Preparation of (2-Allylaryloxo)ruthenium(II) Compounds.** (2-Allylphenoxo)ruthenium(II) compound **1a** was prepared by a conventional metathetical reaction of $RuCpCl(PPh_3)_2$ with potassium 2-allylphenoxide in THF at 50 °C (Scheme 3).[9] 2-Allylphenoxo compound **1a** was isolated as

**Scheme 3**




red crystals as the bis(phosphine) species[11] $RuCp[OC_6H_4(CH_2CH{=}CH_2\text{-}2)\text{-}\kappa^1O](PPh_3)_2$, but in solution it constituted an equilibrium with the mono(phosphine) species $RuCp[OC_6H_4(CH_2CH{=}CH_2\text{-}2)\text{-}\kappa^1O,\eta^2C,C'](PPh_3)$ (**2a**) by releasing one of the $PPh_3$ ligands followed by an $\eta^2$ coordination of the allylic moiety. In order to reveal the electronic and steric effects in this reaction, we have newly prepared a series of (2-allylaryloxo)ruthenium(II) with substituents at either the 4- or 6-position. These compounds **2b–i** were isolated as red to orange crystals in 27–64% yields as moderately air-sensitive compounds and were characterized by $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy as well as elemental analysis. Interestingly, all these compounds were obtained as mono(phosphine) species with an $\eta^2$ coordination of the allylic moiety: $RuCp[OC_6H_3(CH_2CH{=}CH_2\text{-}2)(R)\text{-}\kappa^1O,\eta^2C,C'](PPh_3)$ (**2**).

As a general feature in the $^1H$ NMR spectrum of **2a–i**, the olefinic protons in the allyl fragment appeared at $\delta$ 2.7–2.9 (1H), 3.1–3.2 (1H), and 5.2–5.7 (1H), suggesting coordination of the C=C bond to the Ru(II) center. Consistently, their benzylic methylene protons resonated inequivalently at $\delta$ 1.6–1.9 (1H) and 2.8–3.2 (1H), showing diastereotopic splitting due to the $\eta^2$ coordination of the allyl group to the Ru(II) center.

It is notable that a pioneering work[12] concerning the reaction of $RuCpClL_2$ with NaOMe or NaOEt is reported not to give $RuCp(OR)L_2$ but gives $RuCpHL_2$, probably due to rapid $\beta$-hydride elimination.[13] The mononuclear (aryloxo)ruthenium(II) complexes with a Cp ligand are unprecedented, and only limited numbers of the related complexes $RuCp^*(OPh)(PMe_3)_2$[14] and $RuTp(OPh)(PMe_3)_2$[15] have been reported.

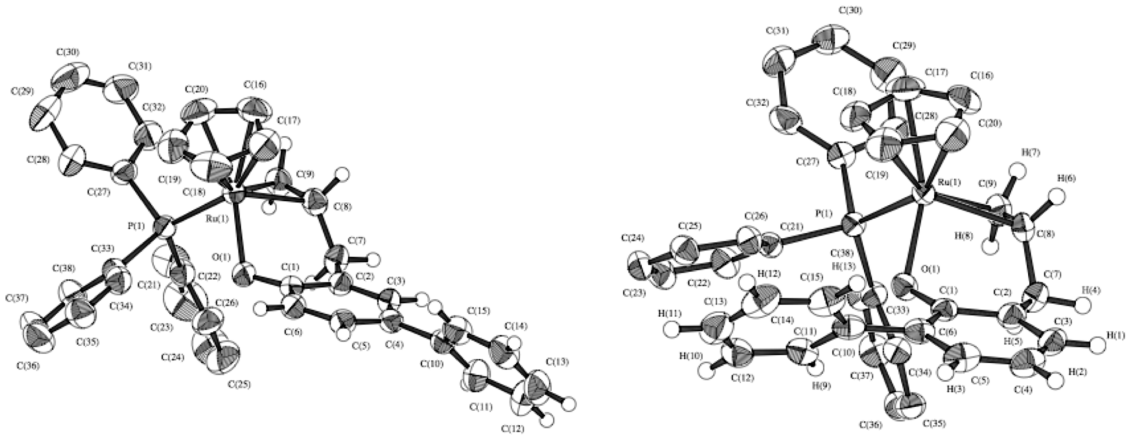
**2. Molecular Structures of (2-Allylaryloxo)ruthenium(II) Compounds.** Compounds **2b,d–f,h,i** were characterized by single-crystal X-ray diffraction. Those molecular structures are basically similar to each other; the ORTEP drawings of **2d,i** are depicted in Figure 1, and the other structures are deposited in the Supporting Information. Data collection and refinement parameters are given in Table 1.

All these compounds adopt a three-legged piano-stool structure with a Cp ligand, aryloxo oxygen, $\eta^2$-allylic fragment, and $PPh_3$. No significant differences were found in the bonds Ru(1)–P(1) (2.3097–2.3267 Å), Ru(1)–O(1) (2.107–2.1410 Å), Ru–C(8) (2.180–2.192 Å), Ru(1)–C(9) (2.195–2.218 Å), O(1)–C(1) (1.316–1.340 Å), C(2)–C(7) (1.496–1.508 Å), C(7)–C(8) (1.494–1.512 Å), and C(8)–C(9) (1.388–1.411 Å) and in the bond angles Ru(1)–O(1)–C(1) (114.9–121.29°), C(2)–C(7)–C(8) (110.8–115.2°), and C(7)–C(8)–C(9) (121.7–123.5°). The substituents do not affect these bond distances and angles in **2b–i**.

**3. Equilibrium between 1 and 2.** As noted, compound **1a** was isolated as the bis(phosphine) species but the other substituted (2-allylaryloxo)ruthenium(II) complexes **2b–i** were isolated as the mono(phosphine) complexes having an $\eta^2$ coordination of the 2-allyl group. In benzene solution, **1a** constituted an equilibrium with **2a**, and this equilibrium was shifted to the **2a** side at room temperature (**2a**/**1a** = 90/10 at 298 K, initial concentration of **1a** 37.5 mM). The equilibrium constant $K_1$ ($K_1 = [\mathbf{2a}][PPh_3]/[\mathbf{1a}]$) at 298 K was estimated to be 0.31 M (Scheme 3). The van't Hoff plot shows the thermodynamic parameters as follows: $\Delta H = 29 \pm 2$ kJ mol$^{-1}$, $\Delta G_{298} = 3 \pm 4$ kJ mol$^{-1}$, $\Delta S = 87 \pm 5$ J mol$^{-1}$ K$^{-1}$. These thermodynamic data suggest slightly endothermic properties, and the positive entropy change is consistent with the liberation of a $PPh_3$ ligand from **1a**.

Since **2b–i** were isolated as the mono(phosphine) compounds, we studied the reactions of **2b–i** with $PPh_3$ in


dx.doi.org/10.1021/om200974c | Organometallics 2012, 31, 381–393



**2d** **2i**

**Figure 1.** ORTEP drawings of 2-allyl-4-phenylphenoxo (**2d**) and 2-allyl-6-phenylphenoxo (**2i**) complexes of Ru(II). Hydrogen atoms, except those of the aryloxo fragment, are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. For compound **2i**, two crystallographically independent molecules were present in the unit cell and only one of them is depicted because they had similar structures.

**Table 1. Data Collection and Refinement Parameters for X-ray Structures of 2d,i**

| | 2d | 2i |
|---|---|---|
| empirical formula | $C_{38}H_{33}OPRu$ | $C_{38}H_{33}OPRu$ |
| formula wt | 637.72 | 637.72 |
| color | orange | red |
| cryst size (mm) | 0.63 × 0.15 × 0.11 | 0.98 × 0.76 × 0.54 |
| cryst syst | monoclinic | monoclinic |
| $a$ (Å) | 11.8410(6) | 20.4154(5) |
| $b$ (Å) | 9.9843(5) | 14.0039(4) |
| $c$ (Å) | 30.037(2) | 20.9509(6) |
| $\beta$ (deg) | 97.753(4) | 93.3277(17) |
| $V$ (Å$^3$) | 3518.6(4) | 5979.7(3) |
| space group | $P2_1/n$ | $P2_1/n$ |
| $Z$ | 4 | 8 |
| radiation | Mo K$\alpha$ | Mo K$\alpha$ |
| temp (K) | 200.0 | 200.0 |
| R1 (wR2) | 0.0541 (0.1908) | 0.0437 (0.1122) |
| GOF | 1.086 | 1.083 |

benzene. With the addition of 5 equiv of $PPh_3$ to a benzene-$d_6$ solution of **2d** at 20 °C as an example, a set of new resonances assignable to the bis(phosphine) complex **1d** was observed by NMR spectroscopy and the system reached a steady-state equilibrium within 1 h. In the $^{31}P\{^1H\}$ NMR spectrum, a new singlet appeared at $\delta$ 40.13. The $^1H$ NMR spectrum involved a new 5H singlet at $\delta$ 4.22 assignable to the Cp ligand and a set of doublets at $\delta$ 3.07 (d, $J$ = 6.9 Hz, 2H), 5.09 (d, $J$ = 9.6 Hz, 1H), 5.11 (d, $J$ = 17.0 Hz, 1H), and 6.12 (ddt, $J$ = 17.0, 9.6, 6.9 Hz, 1H) assigned as the equivalent benzylic methylene, terminal methylene (cis to benzyl), terminal methylene (trans to benzyl), and methine proton in the uncoordinated allyl group, respectively. Although the aromatic resonances are obscured by the resonances of **2d**, these resonances are assigned as **1d**. The **2d**/**1d** ratio under these conditions was 69/31. On the basis of the reactions of **2b**−**i** with 5 equiv of $PPh_3$ in benzene-$d_6$ at 20 °C, the equilibrium constant $K_1$ ($K_1$ = [**2**][$PPh_3$]/[**1**]) was estimated as shown in Table 2.

The 4-substituted 2-allylphoxo compounds **2b**−**f** yielded bis(phosphine) compounds **1b**−**f** by the addition of $PPh_3$.

**Table 2. Reaction of 2b−i with 5 equiv of $PPh_3$ in Benzene-$d_6$ at 20 °C**

| starting compd | R | 2/1 | $K_1$[a] (M) |
|---|---|---|---|
| **2b** | 4-MeO | 73/27 | 0.21 |
| **2c** | 4-Me | 75/25 | 0.24 |
| **2d** | 4-Ph | 69/31 | 0.17 |
| **2e** | 4-Br | 70/30 | 0.18 |
| **2f** | 4-$NO_2$ | 47/53 | 0.066 |
| **2g** | 6-MeO | 100/0 | ∞ |
| **2h** | 6-Me | 100/0 | ∞ |
| **2i** | 6-Ph | 100/0 | ∞ |

[a] $K_1$ = [**2**][$PPh_3$]/[**1**]. Conditions: initial concentration of **2** 0.018 M.

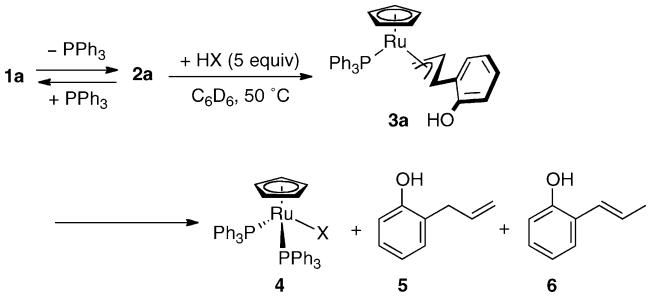
Notably, there is not a great deal of difference in the equilibrium constants $K_1$ among **1a** ($K_1$ = 0.38 M) and **2b**−**f** ($K_1$ = 0.24−0.066 M). Thus, the reason **2b**−**e** have been isolated as mono(phosphine) compounds and **1a** as a bis(phosphine) compound does not arise from the equilibrium constant $K_1$. This is probably due to the relative solubility between **1** and **2** in their recrystallization process. In contrast to **2b**−**f**, **2g**−**i**, having a substituent at the 6-position, did not react with $PPh_3$ under these conditions at all. This sharp contrast presumably arises from the steric repulsion between the $PPh_3$ ligand and the substituent at the 6-position in their putative bis(phosphine) compounds **1**.

**4. Reactions of (2-Allylaryloxo)ruthenium(II) with a Series of Brønsted Acids.** The isolated complex **1a** was treated with a series of Brønsted acids, and the reactions were monitored by NMR spectroscopy. These reactions are summarized in Scheme 4 and Table 3.[16]

The product was the $\eta^3$-allylic complex **3a** when an equilibrium mixture of **1a** and **2a** was treated with weak acids (entries 1−12). In the presence of the stronger acids, **1a**/**2a** converted into compound **4** as the dominant product with the formation of 2-allylphenol (**5**) and (*E*)-2-propenylphenol (**6**) (entries 13−23). In these cases, the reaction proceeded instantly and **3a** was not observed at all. However, because treatment of the isolated $\eta^3$-allylic complex **3a** with these strong acids consistently gave comparable results (entries 14, 17, 19, 21 and 23), **3a** should be formed as the initial product and then **3a** was successively decomposed by protonation to give **4**−**6**.


dx.doi.org/10.1021/om200974c | *Organometallics* 2012, 31, 381−393

**Scheme 4**




It is interesting to note that the acidolyses of **1a**/**2a** by $CF_3CO_2H$ ($pK_a$ = 0.2) and $HPF_6$ ($pK_a$ = −20) dominantly produced **6** (entries 13 and 22), although those by HCl ($pK_a$ = −7), HBr ($pK_a$ = −9), and HI ($pK_a$ = −11) mainly gave **5**. Thus, the product selectivity between **5** and **6** could not be explained by their $pK_a$ values. When the acidolysis by $CF_3CO_2H$ was performed in the presence of $[Ph_3P{=}N{=}PPh_3]Cl$ ($PPN^+Cl^-$) as a source of $Cl^-$, the major product became **5** (entry 15). One of the differences in these reactions is the nucleophilicity between $CF_3CO_2^-$ and $Cl^-$. The nucleophilicity is markedly affected by the steric influence of the anion,[17] and $Cl^-$ is considered to be a better nucleophile than $CF_3CO_2^-$. Thus, the regioselectivity in the protonation might be determined by the nucleophilicity of the counteranion. This prompted us to further investigate this acidolysis.

In order to clarify the acidolysis mechanism, reactions of **1a**/**2a** and **3a** with $CF_3CO_2D$ were performed in the presence or absence of $Cl^-$ (Scheme 5).[18]

The acidolysis of an equilibrium mixture of **1a**/**2a** by 5 equiv of $CF_3CO_2D$ (97 atom % D) exclusively yielded 2-propenylphenol (**6**-*d*), in which the deuterium was incorporated in **6**-*d* at the methyl (0.70D) and benzylic methine (0.25D) positions. In the presence of $PPN^+Cl^-$, 2-allylphenol (**5**-*d*) was formed in 21% yield, where exclusive deuterium incorporation at the benzylic methylene (0.91D) in **5**-*d* was observed. In this case, the dominant product **6**-*d* was also deuterated at the methyl group (0.76D) but the deuterium incorporation at the benzylic methine moiety was obscured by the signal overlapping. When **1a**/**2a** was treated with DCl in deuterated water (deuterium content was undetermined), 2-allylphenol (**5**-*d*) was dominantly formed. In this case, deuterium was selectively incorporated at the benzylic methylene position (0.37D), although the deuterium content in **5** was quite low.[19] In the presence of DCl, the deuterium content in **6**-*d* could not be determined because of the peak broadening. When a mixture of isolated $\eta^3$-allyl complex **3a** and 1 equiv of $PPh_3$ was treated with these acids, similar results were obtained. Thus, **5**-*d* and **6**-*d* starting from **1a**/**2a** are likely to be formed by the acidolysis of the initial product **3a**. In addition, the products by acidolyses of **1a**/**2a** or **3a** with $CF_3CO_2D$ contained one deuterium atom in the allylic fragment in total. This means that the deuteration process is irreversible. Taking into account of all these facts, the protonation mechanism given in Scheme 6 is proposed. The protonation of **3a** at the Ru center initiates this reaction to give intermediate **B**. The resulting hydride group at the cationic ruthenium migrates to the $\eta^3$-allylic moiety, giving either **C** or **D**. The present isotope labeling study shows exclusive incorporation of deuterium at the benzylic position in 2-allylphenol (**5**), which is formed only in the presence of chloride anion. On the other hand, in the absence of chloride anion,

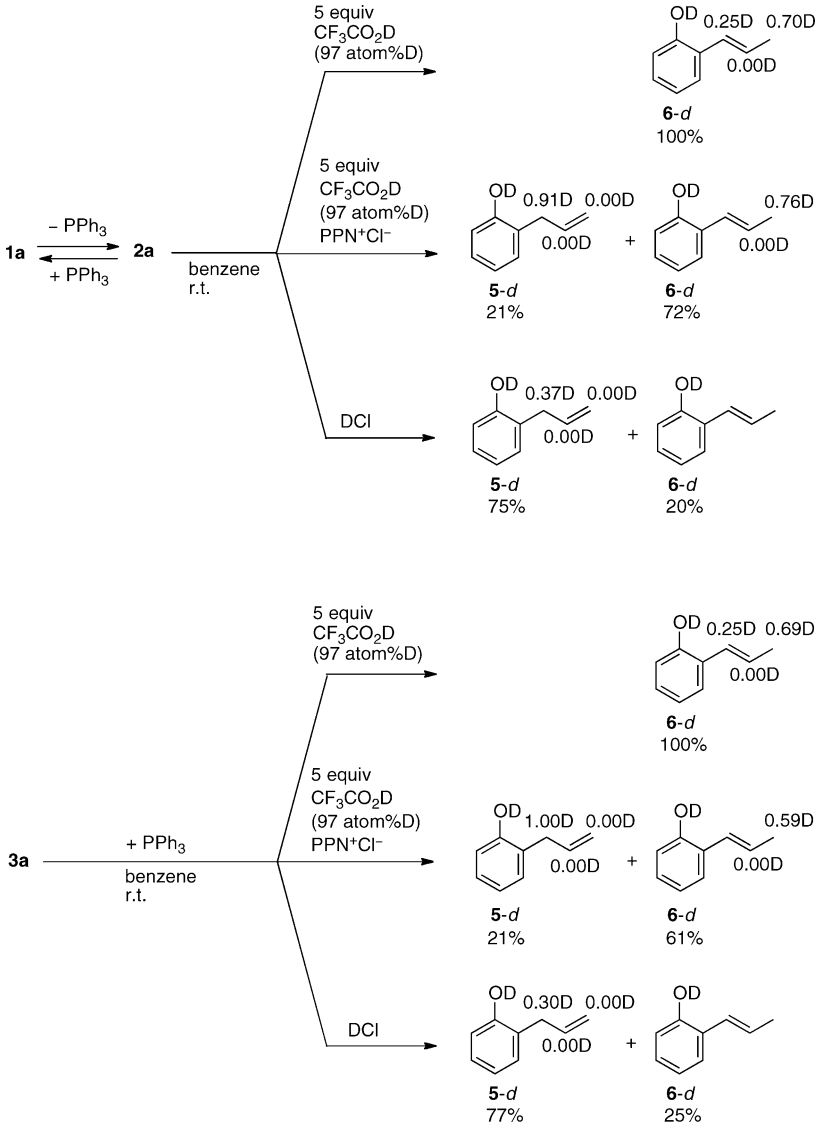
**Table 3. Reactions of 1a and 2a with Brønsted Acids**[a]

| | | | | yield (%) | | | |
|---|---|---|---|---|---|---|---|
| entry | Brønsted acid (HX) | $pK_a$ | time (h) | **3a** | **4** | **5** | **6** |
| 1 | MeOH | 15.5 | 24 | 28 | 0 | 0 | 0 |
| 2[b] | $ClCH_2CH_2OH$ | 14.31 | 23 | 53 | 40 | 59 | 0 |
| 3 | diethyl malonate | 13.3 | 104 | 44 | nd[h] | 0 | 0 |
| 4 | $CF_2HCF_2CH_2OH$ | 12.74 | 2.0 | 94 | nd[h] | 0 | 0 |
| 5 | $CF_3CH_2OH$ | 12.37 | 3.9 | 92 | nd[h] | 0 | 0 |
| 6 | ethyl acetylacetate | 10.68 | 57 | 88 | nd[h] | 3 | 0 |
| 7 | $MeNO_2$ | 10.29 | 21 | 84 | nd[h] | 0 | 0 |
| 8 | 2-allylphenol | 10.23 | 1.7 | 96 | 0 | 0 | 0 |
| 9 | phenol | 10.0 | 0.9 | 98 | 0 | 0 | 0 |
| 10[c] | $(CF_3)_2CHOH$ | 9.3 | instant | 68 | 17 | 17 | 0 |
| 11 | acetylacetone | 8.24 | 21 | 84 | nd[h] | 0 | 0 |
| 12[d] | 2,4,6-trichlorophenol | 6.2 | 0.2 | 84 | 0 | 0 | 0 |
| 13 | $CF_3CO_2H$ | 0.2 | instant | 0 | 85 | 0 | 76 |
| 14[e] | $CF_3CO_2H$ | 0.2 | instant | 0 | 96 | 0 | 70 |
| 15[f] | $CF_3CO_2H$ | 0.2 | instant | 0 | 88 | 64 | 33 |
| 16[g] | HCl | −7 | instant | 0 | 100 | 83 | 17 |
| 17[e,g] | HCl | −7 | instant | 0 | 99 | 82 | 14 |
| 18[g] | HBr | −9 | instant | 0 | 98 | 92 | 0 |
| 19[e,g] | HBr | −9 | instant | 0 | 99 | 95 | 2 |
| 20[g] | HI | −11 | instant | 0 | 97 | 97 | 0 |
| 21[e,g] | HI | −11 | instant | 0 | 85 | 95 | 2 |
| 22[d,g] | $HPF_6$ | −20 | instant | 0 | nd[h] | 28 | 58 |
| 23[d,e,g] | $HPF_6$ | −20 | instant | 0 | nd[h] | 0 | 73 |

[a]Conditions: solvent benzene-$d_6$ (600 μL), **2a** 0.012 mmol, acid 0.06 mmol (5 equiv). [b]At 30 °C. [c]Room temperature. [d]Solvent acetone-$d_6$. [e]A mixture of **3a** and 1 equiv of $PPh_3$ was employed instead of **2a**. [f]$[Ph_3P{=}N{=}PPh_3]Cl$ (0.016 mmol) was added. [g]Excess amout of acid. [h]Not determined but unknown product was formed.


dx.doi.org/10.1021/om200974c | *Organometallics* 2012, 31, 381–393

**Scheme 5**




exclusive formation of 2-propenylphenol (**6**) is observed, where the deuterium atom is distributed in both the terminal and benzylic positions. Thus, we propose a rapid equilibrium between **B** and **C** and the highly nucleophilic chloride anion rapidly attacks the cationic Ru(II) center in **C** to give **E** followed by rapid release of 2-allylphenol. In the absence of chloride anion, **D** is slowly formed from the rapid equilibrium between **B** and **C**, and finally **D** releases 2-propenylphenol.[20] The spontaneous release of 2-propenylphenol from **D** is probably due to the weak coordination of 2-propenylphenol, because it is regarded as a disubstituted olefin.

As a summary of this section, treatment of **1a**/**2a** with relatively weak Br$\phi$nsted acids induced isomerization to the ($\eta^3$-allylic)ruthenium(II) **3a** and further protonation occurred when strong acid was employed.

**5. Association of (2-Allylphenoxo)ruthenium(II) with a Br$\phi$nsted Acid.** As we have described above, treatment of (2-allylphenoxo)ruthenium(II) complex **1a**/**2a** with weak Br$\phi$nsted acid produces ($\eta^3$-allylic)ruthenium(II) **3a**. For a detailed investigation of this process, the $^1$H NMR spectra of **1a**/**2a** (9/91; 0.020 M) were monitored at various concentrations of 2,2,2-trifluoroethanol (TFE) in benzene-$d_6$ at 30 °C.

One of the benzylic methylene protons characteristically shifted downfield upon addition of TFE and the other resonances assignable to **2a** basically remained unchanged (Figure 2). Meantime, the hydroxo resonance of the added TFE shifted upfield upon increasing the concentration, and it finally came closer to the free TFE resonance ($\delta$ 0.99) by further addition of TFE. These phenomena suggest the presence of a rapid associative equilibrium between **2a** and TFE. This chemical shift change was evaluated by a Skatchard plot, giving a linear relationship between $\delta_{obs} - \delta_{2a}$ and $(\delta_{obs} - \delta_{2a})/[TFE]$, where $\delta_{obs}$ and $\delta_{2a}$ denote the chemical shifts of a benzylic methylene proton in a mixture of **2a** and TFE and in **2a**, respectively (see the Supporting Information).[3b,e] The linear relation means the presence of a rapid associative equilibrium between **2a** and TFE gives a 1/1 adduct (eq 2).

$$\mathbf{2a} + \mathrm{HOR} \overset{K_2}{\rightleftarrows} \mathbf{2a}\cdot\mathrm{HOR} \qquad (2)$$

Similarly, the association constant $K_2$ for the reaction of **2a** with a series of weak Br$\phi$nsted acids were estimated from the $^1$H NMR spectra (Table 4).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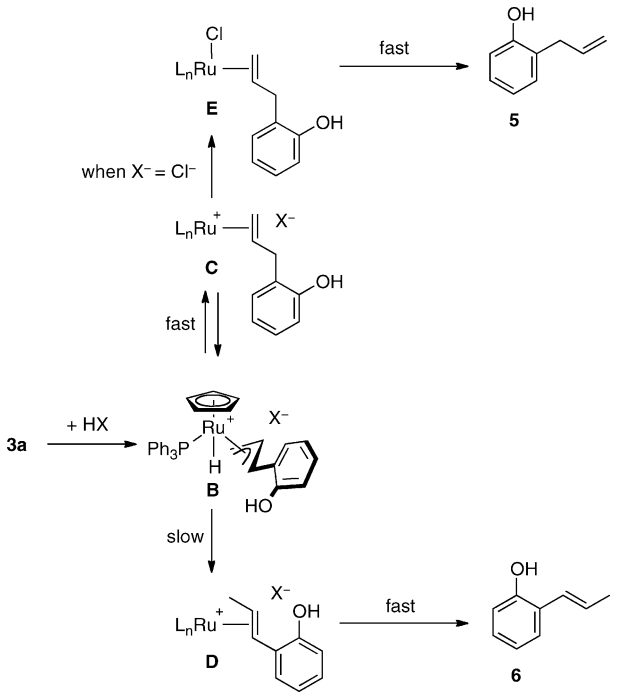
**Scheme 6**



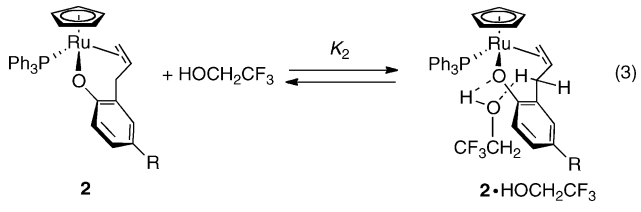

We now have a reliable set of association constants $K_2$ between **2a** and these Brønsted acids in benzene solution, and as shown in Figure 3 these data provide a reasonably straight linear correlation between log $K_2$ and p$K_a$ with a negative slope. According to the linear relationship, a stronger Brønsted acid gives a larger association constant $K_2$.

In order to evaluate the electronic effect of the 2-allylphenoxo fragments in **2**, we measured the association constants of substituted (2-allylphenoxo)ruthenium(II) complexes with TFE in benzene-$d_6$ at 30 °C (Table 5).[21] It is notable that a substituent at the 6-position significantly discourages the association.

Figure 4 shows a linear relationship between log ($K_{2R}/K_{2H}$) and $\sigma_{para}$ value,[22] and the negative $\rho$ value means that this association is promoted by an induction effect.

Taking into account these trends in Brønsted acids and aryloxo moieties, the present association is concluded to be a simple acid–base interaction. From the $^1$H NMR studies, significant and selective downfield shifts for one of the benzylic methylene protons and the hydroxo proton of the acid were observed. Such deshielding is generally caused by an increase in the acidity. We therefore propose the structure of the adduct **2**·HOCH$_2$CF$_3$ in eq 3 being a better description than **A** in Scheme 2.[23] The substituents at the 6-position suppress the association probably because of steric repulsion.

In the previous communication, we assumed this adduct as shown in **A** in Scheme 2, as widely accepted for the interaction between alkoxo and aryloxo ligands in late-transition-metal complexes and Brønsted acids. However, the adduct **A** should be redrawn in the modified form **2**·HOCH$_2$CF$_3$, as shown in eq 3. This is more consistent with all of the observed facts, such as selective downfield shifts of one of the benylic methylene protons and the hydroxo proton of acid in the $^1$H NMR spectrum.



(3)

**6. Kinetic Study for Isomerization of 2-Allylphenoxo to $\eta^3$-Allylic Complex and the Proposed Reaction Pathway.** A benzene solution of **1a**/**2a** (0.0012 M) showed an absorption maximum at 467 nm. Addition of a large excess of 2-allylphenol (250 equiv) as a Brønsted acid to the solution caused a gradual decrease of the absorption band by the formation of **3a**. The time courses of the reaction under various conditions were monitored by UV–vis spectroscopy. The reaction obeyed good pseudo-first-order kinetics. The estimated rate constant ($k_{obs}$) is proportional to the concentration of 2-allylphenol as a Brønsted acid (Figure 5).

In the presence of excess $PPh_3$, the absorption maximum shifted to 425 nm. This blue shift is likely due to the shift of the equilibrium $K_1$ to the **1a** side. Addition of a large excess of 2-allylphenol (250 equiv) to this solution caused a decrease of the absorption band, and the reaction rate also obeyed first-order kinetics. The observed rate constant $k_{obs}$ gradually decreased with an increase of $PPh_3$ concentration (0–900 equiv, 0–1.08 M) (Figure 6). In the presence of 1.08 M (900 equiv) of $PPh_3$, the ratio **1a**/**2a** is estimated to be 74/26.

First of all, reversible dissociation of the $PPh_3$ ligand accompanied by coordination of the C=C bond is established to give a mixture of bis- and mono(triphenylphosphine) complexes **1a** and **2a**. Without addition of $PPh_3$, this equilibrium ($K_1$ = 0.38 M) lies far to the **2a** side under these conditions for the kinetic studies by UV–vis spectroscopy ([**1a**]/[**2a**] = 1/99). There is also an equilibrium ($K_2$ = 12 ± 3 M$^{-1}$) between **2a** and **2a**·HOR in the presence of acid (HOR stands for an acid). It is notable that the rate for constitution of this equilibrium is considered to be much faster than the following C–H bond cleavage reaction, because a merged resonance between **2a** and **2a**·HOR was observed by the $^1$H NMR spectrum before production of **3a**, when HOR was added to the solution containing **2a**.

If **3a** is produced directly from **2a**·HOR, the $k_{obs}$ value should be proportional to the concentration [**2a**·HOR] but not to the concentration of acid [HOR]. When the acid concentration was increased 6-fold, the estimated concentration [**2a**·HOR] would be doubled on the basis of the equilibrium constant $K_2$ ([**2a**]/[**2a**·HOR] was changed from 58/42 to 19/81). In fact, however, a 6-fold increase of acid concentration (0.0613 to 0.360 M) caused an approximately 7-fold increase of the $k_{obs}$ value ($1.0 \times 10^{-4}$ to $7.3 \times 10^{-4}$ s$^{-1}$), as shown in Figure 5. This fact shows that the increase of $k_{obs}$ *value is in direct proportion to the acid concentration [HOR] but not to the concentration of [**2a**·HOR].* Such proportionality can be explained only by the association of the second acid (HOR) to [**2a**·HOR] to give **3a**, as shown in Scheme 7.

With agreement, formation rate equation of **3a** is derived as shown in eq 4 by assuming the C–H bond cleavage steps to be rate-determining.

$$-\frac{d([Ru]_{total}-[\mathbf{3a}])}{dt} = \frac{(k_3K_1K_2 + k_5K_4[PPh_3])[HOR]^2([Ru]_{total} - [\mathbf{3a}])}{(K_1K_2 + K_4[PPh_3])[HOR] + [PPh_3] + K_1} \quad (4)$$

On the basis of a curve-fitting iteration of the experimental data, the association constants of acid to **2a** ($K_2$) and **1a** ($K_4$) and the formation rate constants of **3a** from **2a**·HOR ($k_3$) and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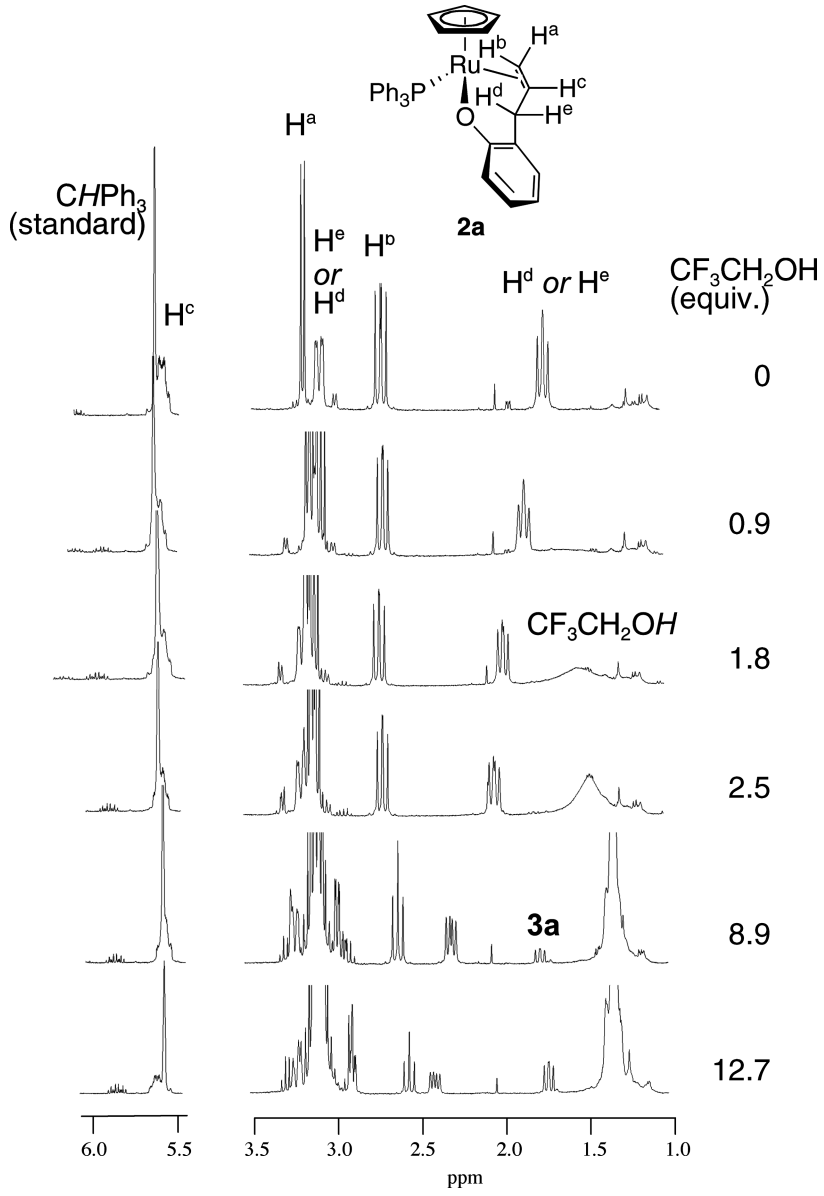



**Figure 2.** $^1$H NMR spectra of the $\eta^2$-allyl group in RuCp[$OC_6H_4(CH_2CH{=}CH_2$-2)-$\kappa^1O,\eta^2C,C'$]($PPh_3$) (**2a**) in the presence of 2,2,2-trifluoroethanol in benzene-$d_6$ at 30 °C. Initial concentration of **1a**/**2a**: 0.020 M. The additional complicated resonances around $\delta$ 3.2 upon addition of 2,2,2-trifluoroethanol are due to the methylene protons in $CF_3CH_2OH$.

**Table 4. Association Constants ($K_2$) between 2a and Brønsted Acid in Benzene-$d_6$ at 30 °C**

| entry | acid | p$K_a$ | $K_2$ ($M^{-1}$) |
|---|---|---|---|
| 1 | 2-allylphenol | 10.23 | 12 ± 3 |
| 2 | $CF_3CH_2OH$ | 12.37 | 8.8 ± 0.3 |
| 3 | $CF_2HCF_2CH_2OH$ | 12.74 | 7.23 ± 0.91 |
| 4 | $CClH_2CH_2OH$ | 14.31 | 1.98 ± 0.48 |
| 5 | MeOH | 15.5 | 0.70 ± 0.36 |
| 6 | EtOH | 16.0 | 0.43 ± 0.27 |

**1a**·HOR ($k_5$) in eq 4 were estimated as follows: $K_2$ = 32 ± 17 $M^{-1}$, $K_4$ = 2 ± 2 $M^{-1}$, $k_3$ = (2.1 ± 1.0) × $10^{-3}$ $M^{-1}$ $s^{-1}$, and $k_5 \approx 0$ $M^{-1}$ $s^{-1}$. This fact means that the bis(phosphine) complex **1a** is inactive to the C−H bond cleavage reaction, which selectively occurs from the mono(phosphine) species **2a**.

To obtain further information on the present C−H bond cleavage reaction, the following experiments were performed in the absence of added $PPh_3$. No retardation was observed for the formation of **3a** in the presence of galvinoxyl as a radical scavenger. When a polar solvent such as acetone or THF was employed in this reaction, the formation rate of **3a** was reduced. An Eyring plot for the formation of **3a** in benzene showed the following kinetic parameters: $\Delta G^{\ddagger}_{298}$ = 91 ± 10 kJ $mol^{-1}$, $\Delta H^{\ddagger}$ = 59 ± 5 kJ $mol^{-1}$, and $\Delta S^{\ddagger}$ = −108 ± 17 J $mol^{-1}$ $K^{-1}$. The large negative entropy of activation is consistent with the association of the second acid with **2a**·HOR.

The observed formation rate constants of **3b**−**i** were similarly estimated by UV−vis spectroscopy. Because complexes **2b**−**i** were isolated as the mono(phosphine) complexes, the term of [$PPh_3$] in eq 4 is deleted and the observed rate constant is expressed as shown in eq 5.

The observed rate constant $k_{obs}$ and the rate for the C−H bond cleavage reaction $k_3$, which can be estimated from eq 5,


dx.doi.org/10.1021/om200974c | *Organometallics* 2012, 31, 381−393

are given in Table 6. As shown in Figure 7, the rate constant $k_3$ is almost independent of the Hammett $\sigma_{para}$ value. We will discuss these features in the next section.

$$k_{obs} = \frac{k_3 K_2 [HOR]^2}{K_2 [HOR] + 1} \quad (5)$$

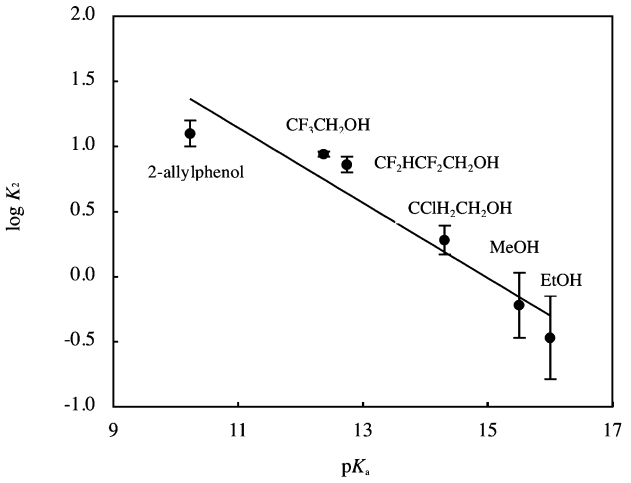



**Figure 3.** Relation between the p$K_a$ value of Br$\phi$nsted acid and association constant $K_2$ in benzene-$d_6$ at 30 °C.

**Table 5. Association Constants ($K_2$) between RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)(R)-$\kappa^1O,\eta^2C,C'$]($PPh_3$) (2) and TFE and Corresponding Hammett $\sigma_{para}$ Values in Benzene-$d_6$ at 30 °C**

| entry | R | $\sigma_{para}$ | $K_2$ ($M^{-1}$) |
|---|---|---|---|
| 1 | 4-MeO | −0.268 | 13 ± 4.4 |
| 2 | 4-Me | −0.170 | 9.0 ± 1.4 |
| 3 | H | 0 | 8.8 ± 0.3 |
| 4 | 4-Ph | 0.009 | 5.2 ± 0.9 |
| 5 | 4-Br | 0.232 | 2.9 ± 0.5 |
| 6 | 6-MeO | | 1.5 ± 0.3 |
| 7 | 6-Me | | ~0 |
| 8 | 6-Ph | | ~0 |

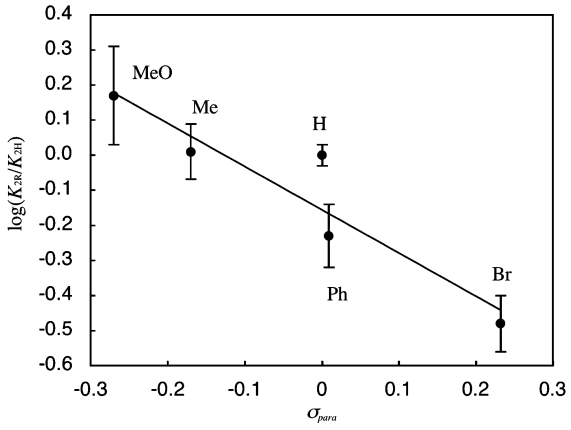



**Figure 4.** Hammett plot for the association constant $K_2$ in benzene-$d_6$ at 30 °C. $K_{2R}$ stands for the association constant $K_2$ of the 2-allylphenoxo complexes with a substituent at the 4-position, and $K_{2H}$ stands for the $K_2$ value of **2a**.

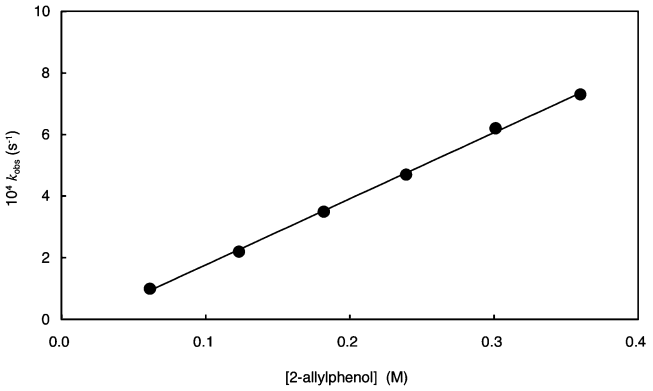



**Figure 5.** Relation between the concentration of 2-allylphenol and $k_{obs}$ for the formation of **3a** in benzene. Conditions: initial concentration of [**1a**/**2a**] 0.0012 M, temperature 30 °C.

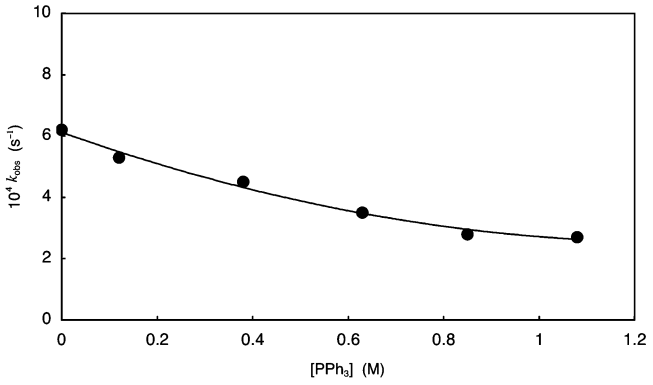
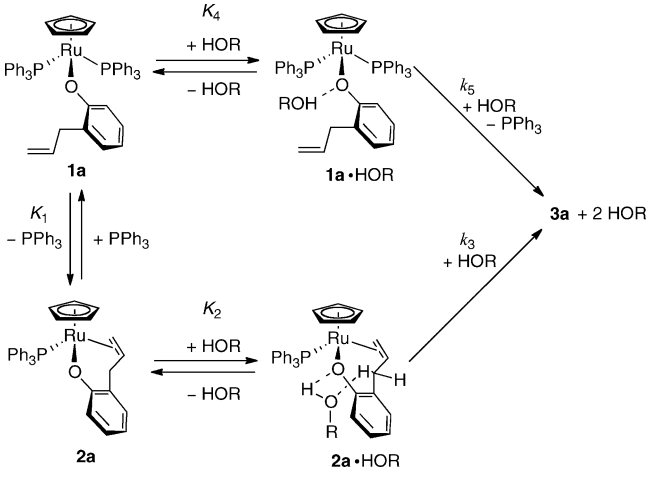



**Figure 6.** Effect of concentration of $PPh_3$ on the observed rate constant $k_{obs}$ in benzene at 29.7 ± 0.1 °C.

**Scheme 7**




**7. Mechanistic Insight into the Acid-Promoted C−H Bond Cleavage Reaction.** In this section, we discuss the C−H bond cleavage step promoted by the acid. The structure of **2**·HOR is deduced to be as shown in Scheme 7. This compound still has lone-pair electrons at the aryloxo oxygen, which enables further association with the second acid. Figure 5 shows an almost linear relation between $k_{obs}$ and the concentration of acid, suggesting the requirement of further association of **2**·HOR with the second acid. Therefore, the successive C−H bond


dx.doi.org/10.1021/om200974c | *Organometallics* 2012, 31, 381−393

**Table 6. Observed Rate Constant $k_{obs}$ and Estimated $k_3$ for Conversion of Complexes 2a–i into 3a–i in Benzene at 30 °C**

| entry | R | $10^4 k_{obs}$ ($s^{-1}$) | $10^3 k_3$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 1 | 4-MeO | 2.62 ± 0.01 | 1.2 ± 0.1 |
| 2 | 4-Me | 3.44 ± 0.01 | 1.6 ± 0.1 |
| 3 | H | 4.62 ± 0.05 | 2.1 ± 1.0 |
| 4 | 4-Ph | 3.20 ± 0.00 | 1.7 ± 0.1 |
| 5 | 4-Br | 2.86 ± 0.00 | 2.0 ± 0.2 |
| 6 | 6-MeO | 3.20 ± 0.00 | 3.6 ± 0.5 |
| 7 | 6-Me | 0.30 ± 0.00 | 0 |
| 8 | 6-Ph | 0.11 ± 0.00 | 0 |

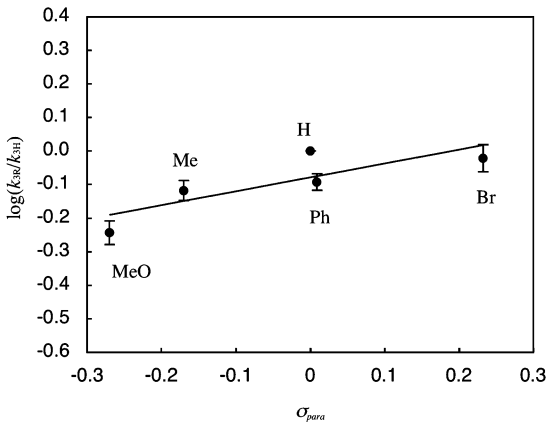
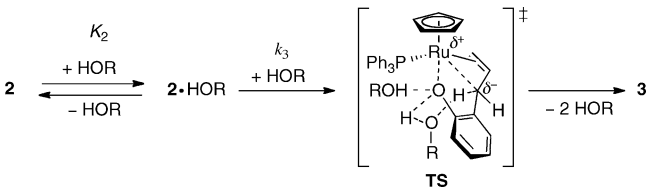



**Figure 7.** Relation between Hammett $\sigma_{para}$ value and the rate constant $k_3$ in benzene at 30 °C. $k_{3R}$ stands for the rate constant $k_3$ for the substituted 2-allylphenoxo complex, and $k_{3H}$ stands for the rate constant $k_3$ for **2a**.

**Scheme 8**

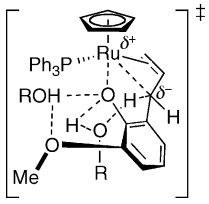



cleavage reaction does occur from **2**·$(HOR)_2$ as shown in Scheme 8.

Although the transition-metal aryloxide/alkoxide complexes are known to have p$\pi$–d$\pi$ interactions, the association of the second acid to **2**·HOR would significantly decrease the p$\pi$–d$\pi$ interaction. Thus, such association is expected to decrease the electron density at the Ru(II) center. On the other hand, we have observed selective deshielding of a benzylic proton by the acid interaction to suggest an increase of the acidity. Therefore, the most probable role of the added second acid is to increase the electrophilicity of the Ru(II) center, as shown in Scheme 8. In agreement, the electron-withdrawing substituents at the 4-position in the aryloxo group would play opposing roles, because those with high induction effects encourage the association with the second acid but they also discourage the electrophilicity of the Ru(II) center at the same time. This hypothesis explains well the small dependence of $k_3$ on the $\sigma_{para}$ value.

A substituent at the 6-position generally discourages the isomerization reaction. Since the association constants of **2g–i** with the first acid $K_2$ are very small or zero, steric repulsion would be the reason for the small (or zero) association constant. However, the fact that **2g**, having a MeO group at the 6-position, shows the fastest rate constant $k_3$ of the C–H bond activation reaction seems to be a puzzling outcome at first sight. We believe that this is exactly a collateral evidence for the structure of transition state **TS** in Scheme 8, because the MeO group at the 6-position would stabilize the second acid association, giving **TS** by hydrogen bonding (Chart 1). A similar

**Chart 1**




internal hydrogen interaction in 6-methoxyphenol was reported.[24] Therefore, we believe the ortho MeO group substantially increases the rate of the C–H bond cleavage reaction step.

The present mechanism can be considered as an electrophilic substitution initiated by an internal base.[25] In fact, there are several studies in which a cleaved hydrogen transfers to the lone pair of an internal oxygen atom by a similar process.[26] However, our studies show that, unlike many pioneering examples, the formal acceptor of the cleaved hydrogen is a conjugate base of the added acid. Although some studies on methane activation by a Pt(bpym) system report the reaction to be inhibited at lower acid concentrations,[27] suggesting that acid promotes the electrophilic substitution mechanism, it still remains largely unknown as to how the added acid promotes the C–H bond activation as Dixneuf and Jutand et al. recently documented.[28] With these points in mind, this work sheds some light on one of these obscured mechanisms.

## ■ CONCLUDING REMARKS

These results presented in this article serve to illustrate that an aryloxo complex of late transition metals associates with Br$\phi$nsted acids and the conjugated base fragment of the acid also has an interaction with a benzylic C–H bond. A new association among the aryloxo oxygen, a benzylic methylene proton, and Br$\phi$nsted acid is proposed. It is interesting that such a weak interaction based on hydrogen bonding promotes the C–H bond cleavage reaction. These findings should give fundamental knowledge about the acid-promoted C–H bond cleavage reaction.

## ■ EXPERIMENTAL SECTION

**General Procedures.** All procedures described in this paper were carried out under a nitrogen or argon atmosphere by use of Schlenk and vacuum-line techniques. Benzene, hexane, toluene, and $Et_2O$ were dried over dry calcium chloride and were distilled over sodium wire under nitrogen using benzophenone ketyl as an indicator. THF was distilled over sodium wire under nitrogen in the presence of benzophenone. Acetone and dichloromethane were dried over Drierite and distilled under nitrogen. Methanol and ethanol were dried over molecular sieves 4A and then distilled under nitrogen over magnesium alkoxide. $C_6D_6$ was dried over sodium wire under reduced pressure, and it was transferred into an NMR tube by vacuum distillation. $RuClCp(PPh_3)_2$ was prepared by a literature method.[29] 2-Allyl-4-methoxyphenol, 2-allyl-4-methylphenol, 2-allyl-4-phenylphenol,


dx.doi.org/10.1021/om200974c | Organometallics 2012, 31, 381–393

2-allyl-4-bromophenol, 2-allyl-4-nitrophenol, 2-allyl-6-phenylphenol, and 2-allyl-6-methoxyphenol were prepared from the corresponding ethers by a Claisen rearrangement.[30] The potassium salts of these 2-allylphenol analogues were prepared by the reaction of the corresponding 2-allylphenol and potassium methoxide.

$^1$H and $^{31}$P{$^1$H} NMR spectra were measured on a JEOL LA300 or a JEOL ECX400P spectrometer. The IR spectra were measured on a JASCO FT/IR410 or FT/IR4100 spectrometer. UV−vis spectra were measured on a Shimadzu UVSpec-1500 instrument. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHN analyzer. The compounds without elemental analyses were characterized by spectroscopic methods.

**RuCp[OC$_6$H$_4$(CH$_2$CH═CH$_2$-2)-$\kappa^1O$](PPh$_3$)$_2$ (1a) and RuCp-[OC$_6$H$_4$(CH$_2$CH═CH$_2$-2)-$\kappa^1O,\eta^2C,C'$](PPh$_3$) (2a).** As a typical example, treatment of RuCpCl(PPh$_3$)$_2$ with potassium 2-allylphenoxide is described in detail. RuCpCl(PPh$_3$)$_2$ (186.9 mg, 0.2574 mmol) was dissolved in THF (4 mL) in a Schlenk tube. A THF solution (5 mL) of potassium 2-allylphenoxide (295.0 mg, 1.713 mmol) was added to the solution, and the reaction mixture was warmed to 50 °C for 2 h. After removal of all volatile materials, the resulting solid was extracted with benzene and the benzene solution was evaporated to dryness. The solid was recrystallized from cold Et$_2$O to give red crystals of **1a** in 75.8% yield (160.8 mg, 0.1952 mmol). IR (KBr, cm$^{-1}$): 3051 (m), 2985(w), 2869 (w), 1957 (vw), 1894 (vw), 1823 (vw), 1634 (w), 1584 (s), 1479 (s), 1469 (s), 1443 (s), 1281 (s), 1088 (m), 741 (s), 695 (s), 529 (s), 516 (s). Anal. Calcd for $C_{50}H_{44}OP_2Ru$: C, 72.89; H, 5.38. Found: C, 72.93; H, 5.14. Complex **1a** constitutes an equilibrium mixture with the mono(phosphine) complex **2a** in a benzene solution. **1a**: $^1$H NMR (300 MHz, $C_6D_6$, 30.0 °C) $\delta$ 3.03 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, benzylic C$H_2$), 4.21 (s, 5H, *Cp*), 5.04 (d, $^3J_{H-H}$ = 9.9 Hz, 1H, C$H_2$═), 5.06 (d, $^3J_{H-H}$ = 16.5 Hz, 1H, C$H_2$═), 6.11 (ddt, $^3J_{H-H}$ = 16.5, $^3J_{H-H}$ = 9.9, $^3J_{H-H}$ = 6.9 Hz, 1H, ═C*H*), 7.6 (m, 6H, P*Ph*$_3$), other aromatic resonances obscured by other aromatic protons assignable to the major species **3c** and liberated PPh$_3$. **2a**: $^1$H NMR (300 MHz, $C_6D_6$, 18.0 °C) $\delta$ 1.84 (dd, $^2J_{H-H}$ = 12.0, $^3J_{H-H}$ = 11.7 Hz, 1H, benzylic C*H*H), 2.78 (dd, $^3J_{H-H}$ = 13.8, $^3J_{H-P}$ = 10.8 Hz, 1H, C$H_2$═), 3.14 (br dd, $^2J_{H-H}$ = 12, $^3J_{H-H}$ = 4 Hz, 1H, benzylic CH*H*), 3.20 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, C$H_2$═), 3.96 (s, 5H, *Cp*), 5.59 (m, 1H, ═C*H*−), 6.81 (td, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.2 Hz, 1H, 4-C$_6H_4$), 6.9 (br.m, 1H, C$_6H_4$), 7.0 (m, 9H, *m*- and *p*-P*Ph*$_3$), 7.26 (t, $^3J_{H-H}$ = 8 Hz, 2H, C$_6H_4$), 7.8 (m, 6H, *o*-P*Ph*$_3$); $^{31}$P{$^1$H} NMR (122 MHz, $C_6D_6$) $\delta$ 48.97 (s).

**RuCp[OC$_6$H$_3$(CH$_2$CH═CH$_2$-2)(OMe-4)-$\kappa^1O,\eta^2C,C'$](PPh$_3$) (2b).** Red crystals, 33% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.90 (br dd, $^2J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 11 Hz, 1H, benzylic C*H*H), 2.78 (dd, $^3J_{H-H}$ = 13.7 Hz, $^3J_{H-P}$ = 11.0 Hz, 1H, CH*H*═), 3.11 (br dd, $^2J_{H-H}$ = 12 Hz, $^3J_{H-H}$ =3 Hz, 1H, benzylic C*H*H), 3.21 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, C*H*H═), 3.61 (s, 3H, 4-O*Me*), 3.99 (s, 5H, *Cp*), 5.56 (m, 1H, ═C*H*-), 6.9−7.2 (m, 12H, *m*- and *p*-P*Ph*$_3$, C$_6H_3$), 7.8−7.9 (m, 6H, *o*-P*Ph*$_3$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): $\delta$ 48.63 (s). IR (KBr, cm$^{-1}$): 1573 (m, $\nu_{C=C}$).

**RuCp[OC$_6$H$_3$(CH$_2$CH═CH$_2$-2)(Me-4)-$\kappa^1O,\eta^2C,C'$](PPh$_3$) (2c).** Red needles, 28% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.88 (br dd, $^2J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 12 Hz, 1H, benzylic C*H*H), 2.42 (s, 3H, 4-*Me*), 2.80 (dd, $^3J_{H-H}$ = 13.7 Hz, $^3J_{H-P}$ = 11.0 Hz, 1H, CH*H*═), 3.12 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 4 Hz, 1H, benzylic C*H*H), 3.24 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, C*H*H═), 3.98 (s, 5H, *Cp*), 5.61 (m, 1H, ═C*H*-), 6.9−7.1 (m, 9H, *m*- and *p*-P*Ph*$_3$), 7.07 (d, $^4J_{H-H}$ = 1.8 Hz, 1H, C$_6H_3$), 7.13 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 2.0 Hz, 1H, C$_6H_3$), 7.18 (d, $^3J_{H-H}$ = 8.3 Hz, 1H, C$_6H_3$), 7.7−7.9 (m, 6H, *o*-P*Ph*$_3$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): $\delta$ 48.63 (s). Anal. Calcd for $C_{33}H_{31}OPRu$: C, 68.85; H, 5.43. Found: C, 68.24; H, 5.94. IR (KBr, cm$^{-1}$): 1571 (w, $\nu_{C=C}$).

**RuCp[OC$_6$H$_3$(CH$_2$CH═CH$_2$-2)(Ph-4)-$\kappa^1O,\eta^2C,C'$](PPh$_3$) (2d).** Red crystals, 45% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.86 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 11 Hz, 1H, benzylic C*H*H), 2.79 (dd, $^3J_{H-H}$ = 14 Hz, $^3J_{H-P}$ = 11 Hz, 1H, CH*H*═), 3.18 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 4 Hz, 1H, benzylic C*H*H), 3.22 (d, $^3J_{H-H}$ = 8.3 Hz, 1H, C*H*H═), 3.98 (s, 5H, *Cp*), 5.60 (m, 1H, ═C*H*−), 6.9−7.1 (m, 9H, *m*- and *p*-P*Ph*$_3$), 7.26 (d, $^3J_{H-H}$ = 8 Hz, 1H, C$_6H_3$), 7.13 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, 4-*Ph*), 7.31 (t, $^3J_{H-H}$ = 7.3 Hz, 2H, 4-*Ph*), 7.58 (d, 1H, $^3J_{H-H}$ = 2 Hz, C$_6H_3$), 7.63 (dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, 1H, C$_6H_3$), 7.77 (d, $^3J_{H-H}$ = 7.3 Hz, 1H, 4-*Ph*), 7.7−7.9 (m, 6H, *o*-P*Ph*$_3$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): $\delta$ 48.78 (s). Anal. Calcd for $C_{38}H_{33}OPRu{\cdot}0.4C_6H_{14}{\cdot}0.1C_6H_8{\cdot}0.3H_2O$: C, 72.21; H, 5.59. Found: C, 72.02; H, 5.37. IR (KBr, cm$^{-1}$): 1597 (w, $\nu_{C=C}$).

**RuCp[OC$_6$H$_3$(CH$_2$CH═CH$_2$-2)(Br-4)-$\kappa^1O,\eta^2C,C'$](PPh$_3$) (2e).** Red crystals, 27% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.62 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 11 Hz, 1H, benzylic C*H*H), 2.69 (dd, $^3J_{H-H}$ = 13.5 Hz, $^3J_{H-P}$ = 11.2 Hz, 1H, CH*H*═), 2.87 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 4 Hz, 1H, benzylic C*H*H), 3.13 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, C*H*H═), 3.99 (s, 5H, *Cp*), 5.39 (m, 1H, ═C*H*−), 6.91 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, C$_6H_3$), 6.9−7.1 (m, 9H, *m*- and *p*-P*Ph*$_3$), 7.34 (d, $^4J_{H-H}$ = 2.8 Hz, 1H, C$_6H_3$), 7.39 (dd, $^3J_{H-H}$ = 8.2 Hz, $^4J_{H-H}$ = 2.8 Hz, 1H, C$_6H_3$), 7.6−7.8 (m, 6H, *o*-P*Ph*$_3$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): $\delta$ 48.62 (s). Anal. Calcd for $C_{38}H_{33}OPRu{\cdot}0.3H_2O$: C, 59.50; H, 4.46. Found: C, 59.94; H, 4.50. IR (KBr, cm$^{-1}$): 1573 (w, $\nu_{C=C}$).

**RuCp[OC$_6$H$_3$(CH$_2$CH═CH$_2$-2)(NO$_2$-4)-$\kappa^1O:\eta^2C,C'$](PPh$_3$) (2f).** Red crystals, 27% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.36 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 12 Hz, 1H, benzylic C*H*H), 2.56 (dd, $^3J_{H-H}$ = 13.5 Hz, $^3J_{H-P}$ =11.1 Hz, 1H, CH*H*═), 2.80 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 3 Hz, 1H, benzylic C*H*H), 3.02 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, C*H*H═), 3.83 (s, 5H, *Cp*), 5.26 (m, 1H, ═C*H*−), 6.71 (d, $^3J_{H-H}$ = 8.7 Hz, 1H, C$_6H_3$), 7.0 (m, 9H, *m*- and *p*-P*Ph*$_3$), 7.6 (m, 6H, *o*-P*Ph*$_3$), 8.21 (d, $^4J_{H-H}$ = 3.0 Hz, 1H, C$_6H_3$), 8.34 (dd, $^3J_{H-H}$ = 8.9 Hz, $^4J_{H-H}$ = 2.9 Hz, 1H, C$_6H_3$). $^{31}$P{$^1$H} NMR (122 MHz, $C_6D_6$): $\delta$ 49.1 (s). Anal. Calcd for $C_{32}H_{28}NO_3PRu$: C, 63.36; H, 4.65; N, 2.31. Found: C, 63.87; H, 4.84; N, 2.39. IR (KBr, cm$^{-1}$): 1590 (m, $\nu_{C=C}$).

**RuCp[OC$_6$H$_3$(CH$_2$CH═CH$_2$-2)(OMe-6)-$\kappa^1O:\eta^2C,C'$](PPh$_3$) (2g).** Red crystals, 63% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.97 (br dd, $^2J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 9 Hz, 1H, benzylic C*H*H), 2.83 (dd, $^3J_{H-H}$ = 13.3 Hz, $^3J_{H-P}$ = 11.0 Hz, 1H, CH*H*═), 3.11 (br dd, $^2J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 3 Hz, 1H, benzylic C*H*H), 3.21 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, C*H*H═), 3.74 (s, 3H, 6-O*Me*), 3.83 (s, 5H, *Cp*), 5.61 (m, 1H, ═C*H*−), 6.69 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, C$_6H_3$), 6.8−7.2 (m, 11H, *m*- and *p*-P*Ph*$_3$, C$_6H_3$), 7.8−7.9 (m, 6H, *o*-P*Ph*$_3$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): $\delta$ 47.4 (s). Anal. Calcd for $C_{33}H_{31}O_2PRu$: C, 66.99; H, 5.28. Found: C, 66.26; H, 5.92. IR (KBr, cm$^{-1}$): 1584 (m, $\nu_{C=C}$).

**RuCp[OC$_6$H$_3$(CH$_2$CH═CH$_2$-2)(Me-6)-$\kappa^1O:\eta^2C,C'$](PPh$_3$) (2h).** Red crystals, 37% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.86 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 11 Hz, 1H, benzylic C*H*H), 2.61 (s, 3H, 6-*Me*), 2.78 (dd, $^3J_{H-H}$ = 14.0 Hz, $^3J_{H-P}$ = 11.0 Hz, 1H, CH*H*═), 3.19 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 4 Hz, 1H, benzylic C*H*H), 3.22 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, C*H*H═), 3.99 (s, 5H, *Cp*), 5.64 (m, 1H, ═C*H*−), 6.79 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, C$_6H_3$), 7.0 (m, 9H, *m*- and *p*-P*Ph*$_3$), 7.22 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, C$_6H_3$), 7.30 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, C$_6H_3$), 7.8 (m, 6H, *o*-P*Ph*$_3$). $^{31}$P{$^1$H} NMR (122 MHz, $C_6D_6$): $\delta$ 50.0 (s). Anal. Calcd for $C_{33}H_{31}OPRu$: C, 68.85; H, 5.43. Found: C, 68.89; H, 6.16. IR (KBr, cm$^{-1}$): 1587 (m, $\nu_{C=C}$).

**RuCp[OC$_6$H$_3$(CH$_2$CH═CH$_2$-2)(Ph-6)-$\kappa^1O:\eta^2C,C'$](PPh$_3$) (2i).** Red crystals, 64% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.85 (br dd, $^2J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 11 Hz, 1H, benzylic C*H*H), 2.82 (dd, $^3J_{H-H}$ = 14.2 Hz, $^3J_{H-P}$ = 11.0 Hz, 1H, CH*H*═), 3.04 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, C*H*H═), 3.11 (br dd, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 4 Hz, 1H, benzylic C*H*H), 3.85 (s, 5H, *Cp*), 5.51 (m, 1H, ═C*H*−), 6.81 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, C$_6H_3$), 7.0−7.1 (m, 9H, *m*- and *p*-P*Ph*$_3$), 7.23 (br dd, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz, 1H, C$_6H_3$), 7.29 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, 6-*Ph*), 7.40 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, 6-*Ph*), 7.45 (br dd, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz, 1H, C$_6H_3$), 7.6−7.8 (m, 6H, *o*-P*Ph*$_3$), 7.96 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, 6-*Ph*). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): $\delta$ 50.01 (s). Anal. Calcd for $C_{38}H_{33}OPRu$; C, 71.57; H, 5.22. Found: C, 71.78; H, 5.17. IR (KBr, cm$^{-1}$): 1583 (m, $\nu_{C=C}$).

**van't Hoff Plot for Equilibrium between 1a and 2a.** Complex **1a** (12.5 mg, 0.0152 mmol) was dissolved in benzene-$d_6$ (442.6 mL). In the NMR tube a flame-sealed capillary containing a benzene-$d_6$ solution of PMe$_2$Ph was added as an internal standard. The temperature was changed in the range (25.0 − 60.0) ± 0.1 °C, and the concentration of each species was estimated by the $^{31}$P{$^1$H} NMR spectra. The equilibrium constant $K_1$ was defined as $K_1$ = [**2a**][PPh$_3$]/[**1a**]. Before this experiment, the suitable pulse delay for this experiment was determined to


dx.doi.org/10.1021/om200974c | *Organometallics* 2012, 31, 381−393

be 60 s. This system reached equilibrium within 10 min. Thermodynamic parameters were estimated by the van't Hoff plot: $\Delta H = 29 \pm 2$ kJ mol$^{-1}$, $\Delta G_{298} = 3 \pm 4$ kJ mol$^{-1}$, and $\Delta S = 87 \pm 5$ J K$^{-1}$ mol$^{-1}$.

**Reactions of 2b−i with $PPh_3$.** As a typical example, complex **2d** (0.010 mmol) and $PPh_3$ (0.050 mmol) were placed in an NMR tube into which $C_6D_6$ (600 μL) was introduced by vacuum distillation. The $^1$H and $^{31}$P{$^1$H} NMR spectra showed that the reaction mixture reached equilibrium within 1 h and a new species assignable to RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)(Ph-4)-$\kappa^1O$][$PPh_3$)$_2$ (**1d**) was observed along with **2d**. **1d**/**2d** = 31/69. $^1$H NMR (400 MHz, $C_6D_6$, 19.4 °C): δ 3.07 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, benzylic C*H*$_2$), 4.22 (s, 5H, *Cp*), 5.09 (d, $^3J_{H-H}$ = 9.6 Hz, 1H, CH*H*═), 5.11 (d, $^3J_{H-H}$ = 17.0 Hz, 1H, C*H*H═), 6.12 (ddt, $^3J_{H-H}$ = 17.0, 9.6, 6.9 Hz, 1H, ═C*H*), 6.9−7.9 (aromatic protons, obscured by the other aromatic species). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$, 19.5 °C): δ 40.13 (s). Similary, **2b-c**, **2e-f**, and **2g-i** were treated with 5 equiv of $PPh_3$ at room temperature as follows.

**2b**: **1b**/**2b** = 27/73. RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)(OMe-4)-$\kappa^1O$][$PPh_3$)$_2$ (**1b**). $^1$H NMR (400 MHz, $C_6D_6$, 19.6 °C): δ 3.00 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, benzylic C*H*$_2$), 4.13 (s, 5H, *Cp*), 5.06 (br d, $^3J_{H-H}$ = 10 Hz, 1H, CH*H*═), 5.5 (br m, 1H, C*H*H═), 6.06 (ddt, $^3J_{H-H}$ = 17.0, 10.5, 6.9 Hz, 1H, ═C*H*), 6.8−7.9 (aromatic protons, obscured by the other aromatic species). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$, 19.8 °C): δ 39.79 (s).

**2c**: **1c**/**2c** = 25/75. RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)(Me-4)-$\kappa^1O$]-($PPh_3$)$_2$ (**1c**). $^1$H NMR (400 MHz, $C_6D_6$, 20.2 °C): δ 3.02 (d, $^3J_{H-H}$ = 6.4 Hz, 2H, benzylic C*H*$_2$), 4.21 (s, 5H, *Cp*), 5.07 (br d, $^3J_{H-H}$ = 10 Hz, 1H, CH*H*═), 5.6 (br m, 1H, C*H*H═), 6.11 (ddt, $^3J_{H-H}$ = 17.0, 10.1, 6.4 Hz, 1H, ═C*H*), 6.8−7.9 (aromatic protons, obscured by the other aromatic species). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$, 20.4 °C): δ 39.97 (s).

**2e**: **1e**/**2e** = 30/70. RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)(Br-4)-$\kappa^1O$]-($PPh_3$)$_2$ (**1e**). $^1$H NMR (400 MHz, $C_6D_6$, 19.5 °C): δ 3.13 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, benzylic C*H*$_2$), 4.12 (s, 5H, *Cp*), 4.9 (br, 1H, CH*H*═), 5.4 (br, 1H, C*H*H═), 5.9 (br m, 1H, ═C*H*), 6.8−7.8 (aromatic protons, obscured by the other aromatic species). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$, 19.5 °C): δ 40.19 (s).

**2f**: **1f**/**2f** = 53/47. RuCp[$OC_6H_3(CH_2CH{=}CH_2$-2)($NO_2$-4)-$\kappa^1O$]-($PPh_3$)$_2$ (**1f**). $^1$H NMR (400 MHz, $C_6D_6$, 24.8 °C): δ 2.79 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, benzylic C*H*$_2$), 4.08 (s, 5H, *Cp*), 4.94 (dd, $^3J_{H-H}$ = 17 Hz, $^2J_{H-H}$ = 2 Hz, 1H, CH*H*═), 5.00 (dd, $^3J_{H-H}$ = 10 Hz, $^2J_{H-H}$ = 2 Hz, 1H, C*H*H═), 5.84 (ddt, $^3J_{H-H}$ = 16.8, 9.9, 6.6 Hz, 1H, ═C*H*), 6.8−7.8 (aromatic protons, obscured by the other aromatic species), 8.42 (d, $^4J_{H-H}$ = 2.9 Hz, 3H, $C_6H_3$), 8.45 (dd, $^3J_{H-H}$ = 9.0 Hz, $^4J_{H-H}$ = 2.9 Hz, 1H, $C_6H_3$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$, 24.8 °C): δ 40.94 (s).

**2g**: after addition of 5 equiv of $PPh_3$ to a benzene solution of **2h**, neither the chemical shift nor the half-width changed at all. Similarly, **2h,i** did not react with $PPh_3$ at all.

**Reactions of 2a−i with a Brønsted Acid.** *Method a.* Complex **2a** (9.0 mg, 0.011 mmol) and a flame-sealed capillary containing a $CDCl_3$ solution of triphenylmethane as an external standard were placed in an NMR tube into which $C_6D_6$ (550 μL) was added. After the measurement of the first $^1$H NMR spectrum, 5 equiv of 2,2,2-trifluoroethanol (TFE) was added to the solution. The NMR tube was warmed to 50 °C. After 3.9 h, the $\eta^3$-allylic complex RuCp-[$CH_2CHCH\{C_6H_4(OH\text{-}2)\}$-$\eta^3C,C',C'$][$PPh_3$) (**3a**) was produced in 92% yield.

*Method b.* Complex **2** (275.2 mg, 0.3790 mmol) and potassium 2-allylphenoxide (318.3 mg, 1.848 mg) were dissolved in THF (5 mL), and the reaction mixture was warmed to 50 °C for 2 h. All volatile materials were evaporated, and the resulting orange solid was extracted with benzene. The collected benzene solution was filtered through a Celite pad. Complex **2a** readily isomerized to **3a** on Celite. The filtered solution was evaporated to dryness, and the orange solid was recrystallized from cold THF/hexane to give yellow crystals of **3a** in 26% yield (53.2 mg, 0.0947 mmol).

**3a**: $^1$H NMR (300 MHz, $C_6D_6$) δ 1.01 (ddd, $^3J_{H-P}$ = 16, $^3J_{H-H}$ = 10, $^2J_{H-H}$ = 1 Hz, 1H, *anti*-CH*H*), 1.86 (dd, $^3J_{H-H}$ = 10, $^3J_{H-P}$ = 2 Hz, 1H, C*H*Ar), 2.97 (dd, $^3J_{H-H}$ = 7, $^2J_{H-H}$ = 2 Hz, 1H *syn*-CH*H*), 4.12 (s, 5H, *Cp*), 4.62 (tdd, $^3J_{H-H}$ = 10, $^3J_{H-H}$ = 7 Hz, $^3J_{H-P}$ = 1 Hz, 1H, *central*-C*H*), 6.80 (td, $^3J_{H-H}$ = 7, $^4J_{H-H}$ = 1 Hz, 1H, 4-$C_6H_4$), 7.01 (m, 10H, *m*- and *p*-P$Ph_3$ and $C_6H_4$), 7.16 (overlapped with signal due to residual signal of deuterated benzene, $C_6H_4$), 7.40 (d, $^3J_{H-H}$ = 8 Hz, 1H, 6-$C_6H_4$), 7.71 (t, $^3J_{H-H}$ = 10 Hz, 6H, *o*-P$Ph_3$), 8.62 (br s, 1H, O*H*); $^{31}$P{$^1$H} NMR (122 MHz, $C_6D_6$): δ 63.6 (s). Anal. Calcd for $C_{32}H_{29}OPRu$: C, 68.44; H, 5.20. Found: C, 68.62; H, 5.98.

The other $\eta^3$-allylic compounds were treated similarly.

RuCp[$CH_2CHCH\{C_6H_3(OH\text{-}2)(OMe\text{-}4)\}$-$\eta^3C,C',C''$][$PPh_3$) (**3b**): $^1$H NMR (300 MHz, $C_6D_6$) δ 0.97 (br dd, $^3J_{H-P}$ = 15 Hz, $^3J_{H-H}$ = 8.1 Hz, 1H, *anti*-CH*H*), 1.89 (dd, $^3J_{H-P}$ = 11.4 Hz, $^3J_{H-H}$ = 9.3 Hz, 1H, C*H*$C_6H_3$), 2.95 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ =1.5 Hz, 1H, *syn*-C*H*H), 3.46 (s, 3H, O*Me*), 4.14 (s, 5H, *Cp*), 4.61 (br td, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 7 Hz, 1H, *central*-C*H*), 6.7−7.7 (m, 18H, P$Ph_3$, and $C_6H_3$, other aromatic resonances obscured by other aromatic protons in $Ph_3$CH), 7.95 (br, O*H*); $^{31}$P{$^1$H} NMR (122 MHz, $C_6D_6$) δ 63.43 (s).

RuCp[$CH_2CHCH\{C_6H_3(OH\text{-}2)(Me\text{-}4)\}$-$\eta^3C,C',C''$][$PPh_3$) (**3c**): $^1$H NMR (400 MHz, $C_6D_6$) δ 0.98 (br dd, $^3J_{H-P}$ = 17 Hz, $^3J_{H-H}$ = 10 Hz, 1H, *anti*-CH*H*), 1.86 (dd, $^3J_{H-P}$ = 11.4 Hz, $^3J_{H-H}$ = 10.1 Hz, 1H, C*H*$C_6H_3$), 2.20 (s, 3H, *Me*), 2.98 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ =1.4 Hz, 1H, *syn*-C*H*H), 4.15 (s, 5H, *Cp*), 4.63 (br td, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 8 Hz, 1H, *central*-C*H*), 6.9−7.8 (m, P$Ph_3$, and $C_6H_3$, other aromatic resonaces obscured by other aromatic protons in $Ph_3$CH), 8.28 (br, O*H*); $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$) δ 63.27 (s).

RuCp[$CH_2CHCH\{C_6H_3(OH\text{-}2)(Ph\text{-}4)\}$-$\eta^3C,C',C''$][$PPh_3$) (**3d**): $^1$H NMR (400 MHz, $C_6D_6$) δ 1.01 (br dd, $^3J_{H-P}$ = 16.5 Hz, $^3J_{H-H}$ = 9.6 Hz, 1H, *anti*-CH*H*), 1.87 (dd, $^3J_{H-P}$ = 11.4 Hz, $^3J_{H-H}$ = 9.6 Hz, 1H, C*H*$C_6H_3$), 2.97 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ =1.4 Hz, 1H, *syn*-C*H*H), 4.15 (s, 5H, *Cp*), 4.66 (br tdd, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 7 Hz, $^3J_{H-P}$ = 1 Hz, 1H, *central*-C*H*), 6.9−7.8 (m, P$Ph_3$, and $C_6H_3$, 4-*Ph*, other aromatic resonances obscured by other aromatic protons in $Ph_3$CH), the O*H* resonance was not observed; $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$) δ 63.18 (s).

RuCp[$CH_2CHCH\{C_6H_3(OH\text{-}2)(Br\text{-}4)\}$-$\eta^3C,C',C''$][$PPh_3$) (**3e**): $^1$H NMR (400 MHz, $C_6D_6$) δ 0.92 (br dd, $^3J_{H-P}$ = 15.1 Hz, $^3J_{H-H}$ = 8.7 Hz, 1H, *anti*-CH*H*), 1.65 (dd, $^3J_{H-P}$ = 11.4 Hz, $^3J_{H-H}$ = 9.2 Hz, 1H, C*H*$C_6H_3$), 2.87 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 1.4 Hz, 1H, *syn*-C*H*H), 4.06 (s, 5H, *Cp*), 4.35 (br tdd, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 8 Hz, $^3J_{H-P}$ = 1 Hz, 1H, *central*-C*H*), 6.79 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, $C_6H_3$), 6.9−7.3 (m, *m*- and *p*-P$Ph_3$, and $C_6H_3$, other aromatic resonances obscured by other aromatic protons in $Ph_3$CH), 7.49 (1H, d, $^3J_{H-H}$ = 2.8 Hz, 1H, $C_6H_3$), 7.6−7.7 (m, 6H, *o*-P$Ph_3$), the O*H* resonance was not observed; $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$) δ 62.84 (s).

RuCp[$CH_2CHCH\{C_6H_3(OH\text{-}2)(NO_2\text{-}4)\}$-$\eta^3C,C',C''$][$PPh_3$) (**3f**): $^1$H NMR (300 MHz, $C_6D_6$) δ 0.94 (br dd, $^3J_{H-P}$ = 16 Hz, $^3J_{H-H}$ = 9 Hz, 1H, *anti*-CH*H*), 1.53 (br dd, $^3J_{H-P}$ = 14 Hz, $^3J_{H-H}$ = 12 Hz, 1H, C*H*$C_6H_3$), 2.86 (br d, $^3J_{H-H}$ = 7 Hz, 1H, *syn*-C*H*H), 4.02 (s, 5H, *Cp*), 4.33 (br td, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 8 Hz, 1H, *central*-C*H*), 6.70 (d, $^3J_{H-H}$ = 8.7 Hz, 1H, $C_6H_3$), 6.9−7.8 (m, *m*- and *p*-P$Ph_3$, and $C_6H_3$), 8.2 (m, 1H, $C_6H_3$), 9.18 (br, 1H, O*H*); $^{31}$P{$^1$H} NMR (122 MHz, $C_6D_6$) δ 62.61 (s).

RuCp[$CH_2CHCH\{C_6H_3(OH\text{-}2)(OMe\text{-}6)\}$-$\eta^3C,C',C''$][$PPh_3$) (**3g**): $^1$H NMR (300 MHz, $C_6D_6$) δ 1.01 (br dd, $^3J_{H-P}$ = 16 Hz, $^3J_{H-H}$ = 9 Hz, 1H, *anti*-CH*H*), 1.92 (dd, $^3J_{H-P}$ = 11.1 Hz, $^3J_{H-H}$ = 9.9 Hz, 1H, C*H*$C_6H_3$), 2.47 (s, 3H, *Me*), 2.99 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ =1.2 Hz, 1H, *syn*-C*H*H), 4.15 (s, 5H, *Cp*), 4.63 (br tdd, $^3J_{H-H}$ = 10 Hz, $^3J_{H-H}$ = 9 Hz, $^3J_{H-P}$ = 1 Hz, 1H, *central*-C*H*), 6.77 (t, $^3J_{H-H}$ = 7.5 Hz, 1H, $C_6H_3$), 6.9−7.8 (m, P$Ph_3$, and $C_6H_3$, other aromatic resonances obscured by other aromatic protons in $Ph_3$CH), 8.41 (br, 1H, ArO*H*); $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$) δ 63.47 (s).

RuCp[$CH_2CHCH\{C_6H_3(OH\text{-}2)(Me\text{-}6)\}$-$\eta^3C,C',C''$][$PPh_3$) (**3h**): $^1$H NMR (400 MHz, $C_6D_6$) δ 0.96 (br dd, $^3J_{H-P}$ = 16 Hz, $^3J_{H-H}$ = 9 Hz, 1H, *anti*-CH*H*), 1.99 (dd, $^3J_{H-P}$ = 11.7 Hz, $^3J_{H-H}$ = 9.4 Hz, 1H, C*H*$C_6H_3$), 2.96 (d, $^3J_{H-H}$ = 6.4 Hz, 1H, *syn*-C*H*H), 3.41 (s, 3H, O*Me*), 4.13 (s, 5H, *Cp*), 4.73 (br td, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 8 Hz, 1H, *central*-C*H*), 6.55 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, $C_6H_3$), 6.75 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, $C_6H_3$), 6.9−7.8 (m, P$Ph_3$, and $C_6H_3$, other aromatic resonances obscured by other aromatic protons in $Ph_3$CH), 7.98 (br s, O*H*); $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$) δ 63.33 (s).

RuCp[$CH_2CHCH\{C_6H_3(OH\text{-}2)(Ph\text{-}6)\}$-$\eta^3C,C',C''$][$PPh_3$) (**3i**): $^1$H NMR (400 MHz, $C_6D_6$) δ 1.04 (br dd, $^3J_{H-P}$ = 16 Hz, $^3J_{H-H}$ = 9 Hz,


dx.doi.org/10.1021/om200974c | *Organometallics* 2012, 31, 381−393

1H, *anti*-CH*H*), 1.90 (dd, $^3J_{H-P}$ = 11.0 Hz, $^3J_{H-H}$ = 0.9.6 Hz, 1H, C*H*C$_6$H$_3$), 3.00 (d, $^3J_{H-H}$ = 6 Hz, 1H, *syn*-CH*H*), 4.13 (s, 5H, *Cp*), 4.66 (br td, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 8 Hz, 1H, *central*-*CH*), 6.9−7.8 (m, 23H, *m*- and *p*-P*Ph*$_3$, and C$_6$*H*$_3$, *6-Ph*), 8.75 (s, 1H, O*H*); $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$) $\delta$ 63.48 (s).

**Determination of Association Constant between 2 and Brønsted Acid.** An accurately weighed amount of complex **2** (about 10 mg) was placed in an NMR tube, in which C$_6$D$_6$ (550.0 $\mu$L) was added by a hypodermic syringe. The chemical shift of the benzylic proton was measured at 30 °C. TFE was added stepwise into the

$$\frac{(\delta_{obs} - \delta_2)}{[TFE]} = -K_2(\delta_{obs} - \delta_2) + C \qquad (6)$$

sample by a hypodermic syringe, and the chemical shift of the benzylic proton was measured for each time. The association constant $K_2$ was calculated using the Scatchard equation (eq 6), where $\delta_{obs}$ and $\delta_2$ were the observed chemical shift of the benzylic proton and that in the absence of TFE and *C* is a constant.

Under the present conditions, we could not set up the large excess concentration of TFE to avoid rapid transformation to **3**. Therefore, the amount of TFE in the adduct **2**·TFE cannot be ignored under the present conditions and must set off the concentration of **2**·TFE from the [TFE] term. Thus, we measured the $K_2$ value first from which we recalculated the [TFE] term to give the corrected $K_2$ value. By the iteration of this process, we estimated the final $K_2$ value. The measurement data are deposited in the Supporting Information.

**Crystallographic Analyses.** A Rigaku AFC7R-Mercury II diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 75 Å) was used for data collection at 200.0 K. A selected crystal was mounted on a glass capillary by use of Paratone N oil. The collected data were solved by direct methods (SIR92)[31] and refined by a full-matrix least-squares procedure using SHELXL programs[32,28] on CrystalStructure version 3.8.

**2b**: monoclinic, $P2_1/a$ (No. 14), $a$ = 14.818(2) Å, $b$ = 9.6743(12) Å, $c$ = 14.818(2) Å, $\beta$ = 104.7708(18)°, $V$ = 2689.5(6) Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.461 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.671 mm$^{-1}$, crystal of dimensions 0.69 × 0.36 × 0.33 mm, $R$ ($R_w$) = 0.0479 (0.1492), GOF = 1.052.

**2c**: monoclinic, $P2_1/n$ (No. 14), $a$ = 11.8410(6) Å, $b$ = 9.9843(5) Å, $c$ = 30.037(2) Å, $\beta$ = 97.753(4)°, $V$ = 3518.6(4) Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.204 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.516 mm$^{-1}$, crystal of dimensions 0.63 × 0.15 × 0.11 mm, $R$ ($R_w$) = 0.0541 (0.1908), GOF = 1.086.

**2e**: monoclinic, $P2_1/n$ (No. 14), $a$ = 14.794(3) Å, $b$ = 9.6171(18) Å, $c$ = 19.264(4) Å, $\beta$ = 104.841(3)°, $V$ = 2649.3(9) Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.606 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 2.189 mm$^{-1}$, crystal of dimensions 0.58 × 0.39 × 0.16 mm, $R$ ($R_w$) = 0.0452 (0.1413), GOF = 0.941.

**2f**: monoclinic, $P2_1/a$ (No. 14), $a$ = 14.776(4) Å, $b$ = 9.721(2) Å, $c$ = 19.162(5) Å, $\beta$ = 105.616(4)°, $V$ = 2650.9(11) Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.520 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.687 mm$^{-1}$, crystal of dimensions 0.22 × 0.12 × 0.11 mm, $R$ ($R_w$) = 0.0494 (0.1036), GOF = 0.806.

**2h**: orthorhombic, $Pna2_1$ (No. 33), $a$ = 16.8913(15) Å, $b$ = 10.7861(10) Å, $c$ = 14.4438(13) Å, $V$ = 2631.5(4) Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.453 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.681 mm$^{-1}$. crystal of dimensions 0.55 × 0.28 × 0.21 mm, $R$ ($R_w$) = 0.0267 (0.0766). GOF = 0.835

**2i**: monoclinic, $P2_1/n$ (No. 14), $a$ = 20.4154(5) Å, $b$ = 14.0039(4) Å, $c$ = 20.9509(6) Å, $\beta$ = 93.3277(17)°, $V$ = 5979.7(3) Å$^3$, $Z$ = 8, $D_{calcd}$ = 1.417 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.608 mm$^{-1}$, crystal of dimensions 0.98 × 0.76 × 0.54 mm, $R$ ($R_w$) = 0.0437 (0.1122), GOF = 1.083.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Tables and figures giving thermodynamic and kinetic data, ORTEP drawings for **2b,e,f,h**, tables giving crystallographic parameters and data, and CIF files for **2b,d−f,h,i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENTS

Part of this study was financially supported by a Grant-in-Aid for Scientific Research on Innovative Areas "Molecular Activation Directed toward Straightforward Synthesis" from the Ministry of Education, Culture, Science and Technology of Japan. We thank Ms. S. Kiyota for elemental analysis.

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