Acid-Promoted Hydrogen Migration in (2-Allylphenoxo)ruthenium(II) To Form an η^3-Allyl Complex

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*Summary: Treatment of RuCp[$OC_6H_4(CH_2CH{=}CH_2$-2)-κ^1O:η^2C,C'](PPh$_3$) (**3c**) with a Brønsted acid (HX) such as 2-allylphenol results in facile migration of a benzylic proton to the aryloxide, giving the (η^3-allyl)ruthenium(II) complex RuCp[CH_2-$CHCH(C_6H_4OH$-2)-η^3C,C',C''](PPh$_3$) (**4c**). Thermodynamic and kinetic studies suggest that **3c** associates with acid to give **3c**·HX, and further addition of HX to **3c**·HX causes the C−H bond cleavage reaction to give **4c**.*

C−H bond cleavage reactions by ruthenium complexes have been extensively studied, due to their potential utility in organic synthesis.[1] One of the important factors for C−H bond cleavage reaction is prior coordination or binding through an anchoring group to bring the unactivated C−H bond in proximity to the ruthenium center. We previously reported a series of reactions of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) with ortho-substituted phenols in the presence of PMe_3, where protonation of the 1,3,5-COT ligand immediately took place to give the (η^5-cyclooctadienyl)ruthenium(II) species Ru(η^5-C_8H_{11})($SC_6H_3Me_2$-2,6)(PMe_3)$_2$ and [Ru(η^5-C_8H_{11})-(PMe_3)$_3$]$^+$[$OC_6H_3Me_2$-2,6]$^-$.[2] They were key intermediates for the C−H bond cleavage reactions, giving *cis*-Ru[YC_6H_3(2-CH_2)(6-Me)-κ^2Y,C](PMe_3)$_4$ (Y = S, O). The C−H bond cleavage reaction in the (η^5-cyclooctadienyl)ruthenium(II) species prompted us to study isoelectronic (η^5-cyclopentadienyl)ruthenium(II) species. To our surprise, however, mononuclear (aryloxo)ruthenium(II) complexes having a Cp ligand were unprecedented, while limited numbers of related complexes such as RuCp*(OPh)(PMe_3)$_2$,[3] RuTp(OPh)(PMe_3)$_2$,[4,5] and RuCp(NR_2)(dcype) were reported.[6] Thus, we started to prepare a series of RuCp(OAr)(PPh_3)$_2$ complexes. During the course of this study, we found that Brønsted acids promoted an intramolecular C−H bond cleavage reaction of the (aryloxo)ruthenium(II) complex RuCp[$OC_6H_4(CH_2CH{=}CH_2$-2)-κ^1O](PPh_3)$_2$ (**2c**), leading to RuCp[$CH_2CHCH(C_6H_4OH$-2)-η^3C,C',C'']-(PPh_3) (**4c**) under ambient conditions. Herein we report a new type of acid-promoted C−H bond cleavage reaction.

Metathetical reactions of chlorobis(triphenylphosphine)ruthenium(II) (**1**) with potassium aryloxide in THF under ambient conditions gave the corresponding (aryloxo)(cyclopentadienyl)-bis(triphenylphosphine)ruthenium(II) complexes Ru(OAr)Cp-(PPh_3)$_2$ (Ar = C_6H_5 (**2a**), $C_6H_3Me_2$-2,4 (**2b**), 2-allylphenyl (**2c**), 2-propenylphenyl (**2d**), 2-propylphenyl (**2e**), 1-naphthyl (**2f**)) in moderate to high yields (eq 1).[7] These complexes were characterized by ^{1}H and ^{31}P{^{1}H} NMR, IR, and elemental analysis.[8] It is notable that a pioneering work concerning the reaction of $RuCpCl L_2$ with NaOMe or NaOEt was reported to give $RuCpHL_2$ by facile β-hydrogen elimination from the putative (alkoxo)ruthenium(II).[9]

The molecular structure of **2c** has been unequivocally determined by single-crystal X-ray diffraction, giving the formulation as RuCp[$OC_6H_4(CH_2CH{=}CH_2$-2)-κ^1O](PPh_3)$_2$ (**2c**) with no apparent interaction of the allyl moiety with the ruthenium center.[10]

When complex **2c** was dissolved in benzene-d_6, extensive dissociation of a PPh_3 ligand was observed, giving RuCp[OC_6H_4-

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(1) (a) Shilov, A. E. *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, The Netherlands, 1984. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315. (d) *Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R.; Slocum, D. W., Eds.;Advances in Chemistry 230; American Chemical Society: Washington, D.C., 1992. (e) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Påeterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

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(7) Reaction of **1** with the potassium salt of 2,6-xylenol under the same conditions gave a complex mixture involving $RuHCp(PPh_3)_2$. This reaction will be reported elsewhere.

(8) As a typical example, the characterization of **2c** is described. **2c**: ^{1}H NMR (300 MHz, C_6D_6, 30.0 °C) δ 3.03 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, benzylic CH_2), 4.21 (s, 5H, *Cp*), 5.04 (d, $^3J_{H-H}$ = 9.9 Hz, 1H, CH_2=), 5.06 (d, $^3J_{H-H}$ = 16.5 Hz, 1H, CH_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 in **3c** and free PPh_3. ^{31}P{^{1}H} NMR (122 MHz, C_6D_6): δ 40.4 (s). Complex **2c** constitutes an equilibrium mixture with the monophosphine complex **3c**, having a π coordination of the alkenyl group in benzene-d_6 solution (see ref 11). 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.

(9) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747.

(10) Crystallographic and physical data for **2c**: triclinic, $P\bar{1}$ (No. 2), a = 13.898(3) Å, b = 15.542(4) Å, c = 10.008(2) Å, α = 96.38(2)°, β = 110.60(2)°, γ = 88.54(2)°, V = 2010.6(9) Å^3, Z = 2. R (R_w) = 0.0483 (0.0599) and GOF = 1.101.

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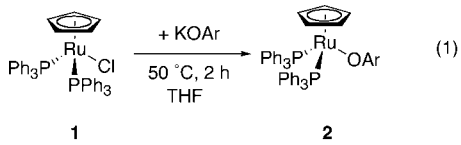
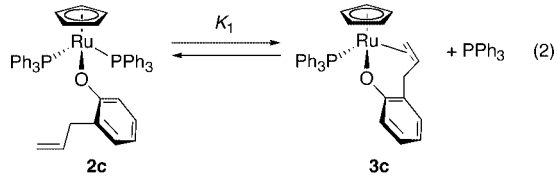


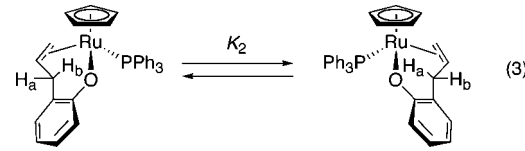
Ar = phenyl (**2a**), 72%
2,4-dimethylphenyl (**2b**), 73%
2-allylphenyl (**2c**), 76%
2-propenylphenyl (**2d**), 91% (*E*/*Z* = 95/5)
2-propylphenyl (**2e**), 59%
1-naphthyl (**2f**), 80%

(CH$_2$CH═CH$_2$-2)-κ^1O:η^2C,C'](PPh$_3$) (**3c**)[11] (eq 2). The ratio of



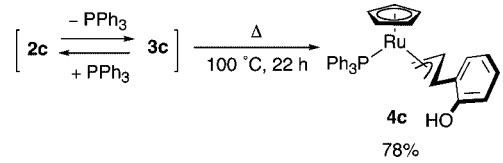
complexes **2c** and **3c** and free PPh$_3$ in benzene-d_6 at 25 °C was estimated as 9:91:92 on the basis of the ^{31}P{^{1}H} NMR spectrum. The ^{1}H NMR spectrum of **3c** shows five correlated resonances at δ 1.86 (dd, 1H), 2.78 (dd, 1H), 3.14 (br dd, 1H), 3.20 (d, 1H), and 5.59 (m, 1H) due to the coordinated 2-allyl moiety, where the signals at δ 1.86 and 3.14 are assignable to the diasterotopic benzylic methylene protons. These results evidently indicate coordination of the 2-allyl moiety to the ruthenium center. In contrast, signals due to the 2-allyl group in **2c** are observed at δ 3.03 (d, 2H), 5.04 (d, 1H), 5.06 (d, 1H), and 6.11 (ddt, 1H), where the two benzylic methylene protons appear equivalently at δ 3.03. When 8 equiv of free PPh$_3$ was added to the benzene solution of the mixture of **2c** and **3c**, the ratio (**2c**/**3c**) changed to 37/63, suggesting that these compounds were in equilibrium. The equilibrium constant K_1 (K_1 = [**3c**][PPh$_3$]/[**2c**]) was estimated as 3.8×10^{-1} M at 303 K in C$_6$D$_6$. Thermodynamic parameters were estimated by a van't Hoff plot of K_1 in the range 25.0−55.0 °C in C$_6$D$_6$ 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 K^{-1} mol^{-1}. These data concerning formation of **3c** from **2c** suggest that the reaction is slightly endothermic and the positive entropy change is consistent with liberation of a PPh$_3$ ligand from **2c**.

When the solution of a mixture of **2c** and **3c** in toluene-d_8 was warmed above room temperature, the signals at δ 1.8 and 3.1, assignable to the diastereotopic benzylic methylene protons of **3c**, gradually broadened and collapsed into the baseline at 80 °C, while other signals due to **3c** remained sharp. Further warming to 100 °C gave one broad signal around δ 2.3−2.5. The PPh$_3$ resonance in the ^{31}P{^{1}H} NMR spectrum and the signals of olefinic protons in the ^{1}H NMR spectrum did not show significant change in this temperature range. This dynamic process is assignable to the exchange between two enantiomers based on coordination of different prochiral faces of the 2-allyl moiety to Ru (i.e., racemization), which arises from rapid dissociation/site exchange/coordination of the 2-allyl moiety (eq 3). On the basis of the coalescence temperature (353 K) of the benzylic methylene protons, the activation free energy $\Delta G^{\ddagger}_{353}$ for this process was estimated as 69 kJ mol^{-1}.



Unexpectedly, heating of the equilibrium mixture in toluene at 100 °C slowly gave rise to the conversion to **4c** in 78% yield for 22 h (Scheme 1).

Scheme 1



The ^{1}H NMR spectrum of **4c** in C$_6$D$_6$ shows typical allylic signals at δ 1.01 (ddd, 1H, anti-C*H*H), 1.86 (dd, 1H, anti-C*H*Ar), 2.97 (dd, 1H, syn-CH*H*), and 4.62 (tdd, 1H, central-C*H*).[12] The hydroxo group resonates at δ 8.6 as a broad peak, which disappears on addition of excess D$_2$O. The molecular structure of **4c** shows a syn arrangement of the 2-hydroxyphenyl group and exo (prone) orientation of the allyl fragment.[13] Such an orientation is also consistent with Jia's DFT calculations of RuCp(η^3-C$_3$H$_5$)(PH$_3$), where the exo (prone) orientation is more stable than the endo (supine) one by 22.6 kJ mol^{-1}.[14]

Treatment of the mixture of **2c** and **3c** with Brønsted acids enhanced conversion to **4c** in C$_6$D$_6$. For example, reaction of the mixture with 5 equiv of PhOH (pK_a = 10.0) in C$_6$D$_6$ at 50 °C for 55 min gave **4c** in 98% yield, with concomitant formation of a trace amount of RuCp(OPh)(PPh$_3$)$_2$ and 2-allylphenol. Similar treatment with 5 equiv of 2-allylphenol (pK_a = 10.23)[15] for 70 min also produced **4c** in 92% yield. With 5 equiv of CF$_3$CH$_2$OH (pK_a = 12.4) for 3.5 h, **4c** was produced in 91% yield, accompanied by formation of RuCpH(PPh$_3$)$_2$ (12%) and 2-allylphenol (7%) under the same reaction conditions. It is notable that when the reaction took place in the presence of 5 equiv of CF$_3$CH$_2$OD (90 atom % D), a deuterium atom was not incorporated in the allylic moiety in **4c** at all. With 5 equiv of MeOH (pK_a = 15.5) and EtOH (pK_a = 16.0) for 1 day, **4c** was obtained in only 19% and 12% yields, respectively. A Brønsted acid with a low pK_a value seems to promote formation of **4c** more effectively. However, a stronger Brønsted acid such as HCl (pK_a = −7) or HPF$_6$ (pK_a = −20) caused protonolysis to liberate 2-allylphenol and the isomer 2-propenylphenol quantitatively.

To obtain insight into the mechanism, the ^{1}H NMR spectra of **2c**/**3c** (9/91; 0.020 M) were monitored at various concentrations of 2-allylphenol (0−0.20 M) in C$_6$D$_6$. The benzylic

(11) **3c**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 18.0 °C) δ 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, CH_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, CH_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$_6$D$_6$) δ 48.97 (s).

(12) **4c**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 1.01 (ddd, $^3J_{H-P}$ = 16, $^3J_{H-H}$ = 10, $^2J_{H-H}$ = 1 Hz, 1H, anti-C*H*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 a syn-CH*H*), 4.12 (s, 5H, *Cp*), 4.62 (tdd, $^3J_{H-H}$ = 10, $^3J_{H-H}$ = 7, $^3J_{H-P}$ = 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*$_3$), 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$_6$D$_6$) 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.

(13) Crystallographic and physical data for **4c**: orthorhombic, $P2_12_12_1$ (No. 61), a = 16.843(4) Å, b = 19.073(5) Å, c = 15.619(5) Å, V = 5011(1) Å^3, Z = 8. R (R_w) = 0.0305 (0.0485) and GOF = 1.244.

(14) Bi, S.; Ariafard, A.; Jia, G.; Lin, Z. *Organometallics* **2005**, *24*, 680.

(15) Stradins, J.; Hasanli, B. *J. Electroanal. Chem. Interfacial Electrochem.* **1993**, *353*, 57.

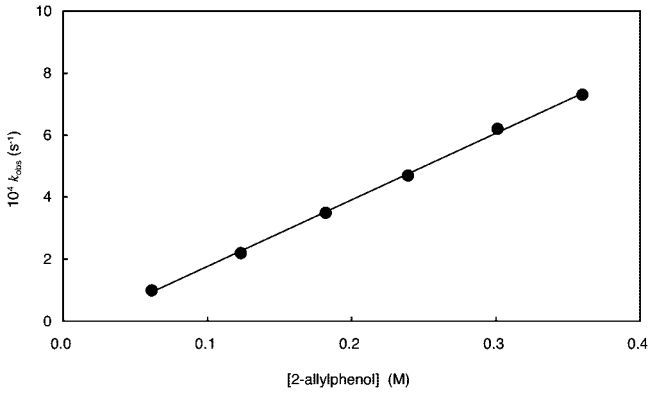
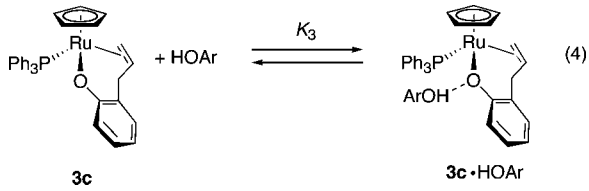


Figure 1. Relation between the concentration of 2-allylphenol and k_{obs} for the formation of **4c** in benzene. Conditions: initial concentration of **2c**/**3c** 0.0012 M, temperature 30 °C.

methylene resonance in **3c** characteristically shifted downfield upon increasing the concentration of 2-allylphenol.[16] Meantime, the hydroxy resonance in 2-allylphenol shifted upfield upon increasing the concentration of 2-allylphenol.[17] This phenomenon suggests a rapid associative equilibrium between **3c** and 2-allylphenol (K_3 = [**3c**·HOAr]/([**3c**][HOAr]) = 12 ± 3 M^{-1} at 30 °C). The most probable interaction between **3c** and 2-allylphenol is hydrogen bonding between the aryloxo oxygen in **3c** and the hydroxo proton in 2-allylphenol, as observed in alkoxo and aryloxo ligands in late-transition-metal complexes (eq 4).[18,19] The downfield shift of the methylene signals in **3c**·HOAr suggests increase of the acidity by association of acid.



The benzene solution of **2c**/**3c** (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 **4c**. 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 (Figure 1).

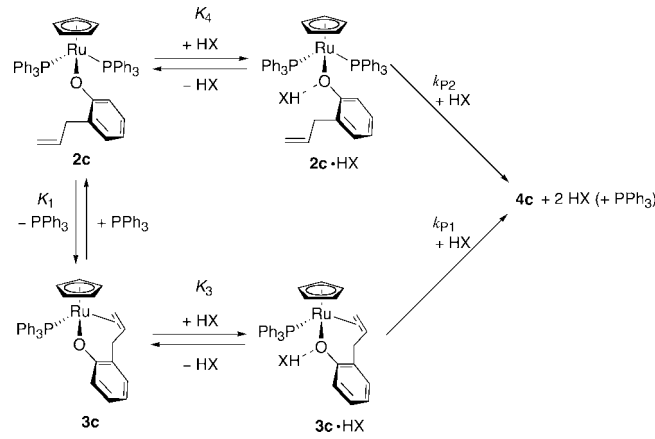
(16) Resonance of the methylene group in **3c** (**2c**/**3c** 0.02 M) in benzene-d_6 at 20 °C: δ 1.98 (0.02 M of 2-allylphenol), δ 2.1 (0.04 M of 2-allylphenol), δ 2.18 (0.06 M of 2-allylphenol), δ 2.28 (0.10 M of 2-allylphenol), δ 2.43 (0.20 M of 2-allylphenol) (cf. methylene resonence in **3c**: δ 1.84).

(17) Resonance of the hydroxy group in added 2-allylphenol in benzene-d_6 at 20 °C: δ 5.52 at 0.02 M, δ 5.05 at 0.10 M, δ 4.73 at 0.20 M in the presence of **2c**/**3c** (0.02 M) (cf. free 2-allylphenol: δ 4.43).

(18) Bickford, C. C.; Johnson, T. J.; Davidson, E. R.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1080.

(19) (a) Yong-Joo, K.; Jae-Young, L.; Osakada, K. *J. Organomet. Chem.* **1998**, *558*, 41. (b) Komiya, S.; Iwata, M.; Sone, T.; Fukuoka, A. *J. Chem. Soc., Chem. Commun.* **1992**, 1109. (c) Simpson, R. D.; Bergman, R. G. *Organometallics* **1992**, *11*, 4306. (d) Osakada, K.; Ohshiro, K.; Yamamoto, A. *Organometallics* **1991**, *10*, 404. (e) Osakada, K.; Kim, Y.; Tanaka, M.; Ishiguro, S.; Yamamoto, A. *Inorg. Chem.* **1991**, *30*, 197. (f) Kim, Y.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096. (g) Osakada, K.; Kim, Y.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *382*, 303. (h) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563.

Scheme 2



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 to the **2c** 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 was also obeyed first-order rate kinetics. The observed rate constant k_{obs} gradually decreased with an increase in added PPh_3 concentration (0−900 equiv: 0−1.08 M). In the presence of 1.08 M (900 equiv) of PPh_3, the ratio **2c**/**3c** is estimated to be 74/26.

From these experimental results, the reaction mechanism for the present acid-promoted isomerization of (2-allylphenoxo) ruthenium(II) to the (η^3-(2-hydroxyphenyl)allyl)ruthenium(II) complex is proposed to be as shown in Scheme 2.

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 **2c** and **3c**. Without addition of PPh_3, this equilibrium (K_1 = 0.38 M) lies far to the **3c** side under these conditions ([**2c**]/[**3c**] = 1/99). There is also an equilibrium (K_3 = 12 ± 3 M^{-1}) between **3c** and **3c**·HX in the presence of acid (HX 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 **3c** and **3c**·HX was observed by the ^{1}H NMR spectrum before producing **4c**, when HX was added into the solution containing **3c**.

If **4c** is produced directly from **3c**·HX, the k_{obs} value should be proportional to the concentration of [**3c**·HX] but not to the concentration of acid [HX]. When the acid concentration was increased sixfold, the estimated concentration of [**3c**·HX] would be doubled on the basis of the equilibrium constant K_3 ([**3c**]/[**3c**·HX] changed from 58/42 to 19/81). In fact, however, a sixfold increase of acid concentration (0.0613 to 0.360 M) caused an approximately sevenfold increase of the k_{obs} value (1.0×10^{-4} to 7.3×10^{-4} s^{-1}), as shown in Figure 1. This fact shows increase of *the k_{obs} value is in direct proportion to acid concentration [HX] but not to the concentration of [3c·HX]*. Such proportionality can be explained only by the association of the second acid (HX) to [**3c**·HX] to give **4c**, as shown in Scheme 2.[20]

On the basis of these considerations, formation rate equation of **4c** is derived as shown in eq 5. From the best calculated curves based on the curve-fitting iteration of experimental data, the association constants of acid to **3c** (K_3) and **2c** (K_4) and the formation rate constants of **4c** from **3c**·HX (k_{P1}) and **2c**·HX

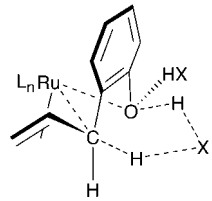
(k_{P2}) in eq 5 were estimated as follows: $K_3 = 32 \pm 17\ M^{-1}$, $K_4 = 2 \pm 2\ M^{-1}$, $k_{P1} = 2.1 \pm 1.0 \times 10^{-3}\ M^{-1}\ s^{-1}$, and $k_{P2} \approx 0\ M^{-1}\ s^{-1}$.

$$-\frac{d([Ru]_{total} - [\mathbf{4c}])}{dt} = \frac{(k_{P1}K_1K_3 + k_{P2}K_4[PPh_3])[HX]^2([Ru]_{total} - [\mathbf{4c}])}{(K_1K_3 + K_4[PPh_3])[HX] + [PPh_3] + K_1} \quad (5)$$

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 **4c** 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 **4c** was reduced.[21] Without addition of PPh_3, the equilibrium between **2c** and **3c** lies far to the **3c** side ([**2c**]/[**3c**] = 1/99). An Eyring plot for the formation of **4c** in benzene showed the following kinetic parameters: $\Delta G^{\ddagger}_{298} = 91 \pm 10\ kJ\ mol^{-1}$, $\Delta H^{\ddagger} = 59 \pm 5\ kJ\ mol^{-1}$, and $\Delta S^{\ddagger} = -108 \pm 17\ J\ mol^{-1}\ K^{-1}$.

These features of the present C−H bond cleavage reaction can be summarized as follows: (a) the C−H bond cleavage reaction proceeds from **3c**·HX, (b) the formation of **3c**·HX is not an intrinsic factor for the C−H bond cleavage reaction and further addition of acid to **3c**·HX is required to give **4c**, (c) no exchange reaction occurred among the benzylic methylene protons and acid during the formation of **4c**, (d) the reaction is not a radical process, (e) polar solvents retard the formation of **4c**, and (f) this reaction shows a large negative entropy of activation. By taking these facts into account, we can propose the most likely process for the present C−H bond cleavage reaction via a concerted mechanism involving a six-membered cyclic transition state (Chart 1).

Chart 1



The kinetic data suggest prerequisite addition of acid to **3c**·HX for the C−H bond cleavage reaction, and the large negative entropy of activation also supports this associative mechanism. The present kinetic data also suggest that formation of **4c** occurs from **3c**·HX, not from **2c**·HX. Probably, coordination of the C═C bond to the ruthenium(II) center would provide a more stable transition state for the C−H bond cleavage reaction. Other mechanisms such as (a) protonation of the ruthenium center followed by abstraction of a benzylic proton by the counteranion and (b) oxidative addition of the benzylic C−H bond followed by reductive elimination between the resulting hydride and aryloxo groups are less likely. Because process a gives a much more polar transition state and process b normally requires coordinative unsaturation, these mechanisms cannot explain the present results. It is notable that several pioneering works were recently reported for the C−H bond activation concerned with the metal−oxygen bond in (hydroxo)ruthenium(II),[22] (hydroxo)iridium(III),[23] (methoxo)iridium(III),[24] (trifluoroethoxo)iridium(III),[25] and (acetato)iridium(III)[26] complexes.

In summary, present work shows the acid-promoted hydrogen migration reaction. It is notable that the addition of acid did not cause simple protonolysis of aryloxoruthenium(II) compound giving a phenol derivative but the acid is employed to form six-membered transition state leading to the formal hydrogen migration from benzylic proton to aryloxo oxygen under ambient conditions. The present result proposes a new C−H bond cleavage mechanism of (aryloxo)ruthenium(II) complexes.

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Supporting Information Available: Text, tables, and figures giving full experimental details involving the preparations and characterizations of **2a**−**f**, **3c**, **3c**·HX, and **4c**, the thermal conversion of **2c**/**3c** to **4c**, treatment of **2c**/**3c** with Brønsted acid, a van't Hoff plot for the equilibrium between **2c** and **3c**, the fluxional behavior in **3c**, the association of **3c** with 2-allylphenol (Scatchard plot), the effect of the concentration of added 2-allylphenol on the observed rate constant, the effect of the concentration of PPh_3 on the observed rate constant, the estimation of equilibrium constants and rate constants, an Eyring plot for the formation of **4c**, and crystallographic analyses of **2c** and **4c** and CIF files giving X-ray crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Although **2c**·HX could not be observed, it is reasonable to propose analogous hydrogen bonding under acidic conditions to give **4c**. However, we believe that this process is not a major process, because preliminary results show that treatment of the DPPE analogue of **2c**, $RuCp(OC_6H_4CH_2CH{=}CH_2)(dppe)$, with 2-allylphenol did not produce the corresponding η^3-allyl complex at all under these conditions. Moreover, the estimated value for k_{P2} is almost 0 $M^{-1}\ s^{-1}$ (see the Supporting Information). However, since we cannot exclude the formation process via **2c**·HX completely, such a possibility is also depicted in Scheme 2.

(21) The observed rate constants are as follows: $6.2 \times 10^{-4}\ s^{-1}$ (benzene), $1.6 \times 10^{-4}\ s^{-1}$ (acetone), and $2.2 \times 10^{-5}\ s^{-1}$ (THF). Conditions: initial concentration of **2c**/**3c** 0.0012 M, 2-allylphenol 250 equiv, temperature 30 °C.

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