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Successive O–H and sp^3 C–H bond activation of *ortho*-substituted phenols by a ruthenium(0) complex

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This paper is dedicated to Professor Martin A. Bennett on his retirement from ANU and in honor of his tremendous contributions to organometallic chemistry.

Abstract

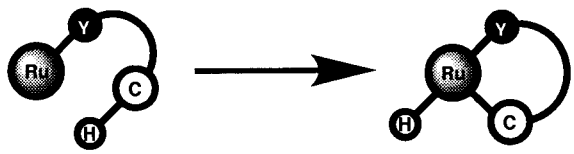
Successive O–H and sp^3 C–H bond activation of *ortho*-substituted phenols has been achieved by the reactions of Ru(1,5-cyclooctadiene)(1,3,5-cyclooctatriene) (**1**) with 2,6-xylenol and 2-allylphenol in the presence of PMe_3 giving oxaruthenacycle complexes such as *cis*-Ru[OC_6H_3(2-CH_2)(6-Me)](PMe_3)$_4$ (**4**) or Ru[OC_6H_4(2-η^3-C_3H_4)](PMe_3)$_3$ (**5**), respectively. They are formed by the initial protonation of Ru(1-2-η^2:5-6-η^2-cycloocta-1,5-diene)(1-4-η^4-cycloocta-1,3,5-triene)(PMe_3) by phenols giving cationic (η^5-cyclooctadienyl)ruthenium(II) complexes [Ru(η^5-C_8H_{11})(PMe_3)$_3$]$^+$[OAr]$^-$·(HOAr)$_n$ [Ar = $C_6H_3Me_2$-2,6 (**2a**), C_6H_4(2-$CH_2CH{=}CH_2$) (**2b**), C_6H_4{2-(*E*)-CH=CHMe} (**2c**), Ph (**2d**); C_6H_4Me-2 (**2e**); C_6H_4(2-$CHMe_2$) (**2f**), and C_6H_4(2-CMe_3) (**2g**)] followed by sp^3 C–H bond cleavage reaction. The molecular structure of **2c** reveals that the cyclooctadienyl group coordinates to the ruthenium center by an η^5-fashion, where one equivalent of (*E*)-2-propenylphenol is associated with aryloxo anion. Further treatment of **2a** and **2c** with PMe_3 results in the formation of oxaruthenacycle complexes to give **4** and **5**, respectively. These facts clearly demonstrate that this sp^3 C–H bond cleavage reaction occurs at a divalent ruthenium center. On the other hand, reactions of **2d**–**g** afford (hydrido)(aryloxo)ruthenium(II) complexes, *cis*-Ru(H)(OAr)(PMe_3)$_4$ [Ar = Ph (**6a**), C_6H_4Me-2 (**6b**), C_6H_4(2-$CHMe_2$) (6c), C_6H_4(2-CMe_3) (**6d**)].

Keywords: Oxaruthenacycle; Successive bond activation; C–H bond activation; Phenols; Ruthenium

1. Introduction

C–H bond activation of organic substrates by transition metal complexes has attracted a great deal of interest for its potential synthetic applications [1]. Low valent ruthenium complexes are particularly paid much attention toward C–H bond activation since Chatt and Davidson revealed oxidative addition of the C–H bond of naphthalene to ruthenium(0) [2]. However, examples for sp^3 C–H bond activation is still very limited to date in comparison with that for sp^2 C–H bond. This may be partly due to difficulty for the former bond in approaching the metal center than the latter. Thus, sp^2 C–H bond activation of triphenylphosphine ligand (orthometallation) [3] as well as metacrylates [4], aromatic ketones [5], benzylalcohol [6], phenols [7] and pyridines [8] suggests importance of prior coordination of substrates to bring a C–H bond near the ruthenium center. Our basic working hypothesis is that when an sp^3 C–H bond is forced to approach a ruthenium center, the bond cleavage reaction should occur as illustrated in Scheme 1.

However, activation of sp^3 C–H bond based on this strategy is still limited for late transition metal com-



Scheme 1.

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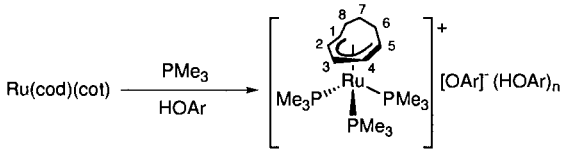
plexes [9]. Published examples involve the sp^3 C–H bond activation of *ortho* substituted aryloxo ligands by Group 6 metal complexes [10], *ortho* substituted phenyl isocyanides by Ru(0) [11], and methyl groups in substituted phosphine [12] and amine ligands [13].

We have previously demonstrated successive C–O and sp^3 C–H bond activation of allyl 2,6-xylyl ether giving an oxaruthenacycle complex with evolution of propylene [14]. This reaction is considered to occur in a stepwise manner by oxidative C–O bond addition to ruthenium(0) giving the aryloxoruthenium(II) complex followed by sp^3 C–H bond cleavage of the *ortho* methyl group. Reaction of a ruthenium(0) complex with *ortho* substituted phenols giving aryloxoruthenium(II) is also considered to be a promising route to sp^3 C–H bond activation, since phenols are know to react with ruthenium to give (hydrido)(phenoxo)ruthenium complexes [15]. Herein we wish to report the reaction of *ortho* substituted phenols by Ru(1,5-cyclooctadiene)(1,3,5-cyclooctatriene) (**1**) in combination with PMe_3, leading to a facile protonation to the 1,3,5-cyclooctatriene ligand followed by sp^3 C–H bond activation of the *ortho* methyl group. A part of this study has been reported as a communication [14].

2. Results and discussion

2.1. Reaction of Ru(1,5-cyclooctadiene)(1,3,5-cyclooctatriene) (1) with phenols

Reaction of **1** with 2,6-xylenol in hexane in the presence of PMe_3 caused immediate deposition of white powder of $[Ru(\eta^5\text{-}C_8H_{11})(PMe_3)_3]^+[OC_6H_3Me_2\text{-}2,6]^-\cdot[HOC_6H_3Me_2\text{-}2,6]$ (**2a**) (Eq. (1)).



Ar = $C_6H_3Me_2$-2,6 (**2a**)
C_6H_4(2-$CH_2CH{=}CH_2$) (**2b**)
C_6H_4{2-(*E*)-CH=CHMe} (**2c**)
Ph (**2d**)
C_6H_4Me-2 (**2e**)
C_6H_4(2-$CHMe_2$) (**2f**)
C_6H_4(2-CMe_3) (**2g**) (1)

The ^{1}H-NMR resonances of **2a** were assigned by ^{1}H–^{1}H COSY as well as by comparison with the spectra of related 1-5-η^5-cyclooctatrienyl complexes such as $Ru(1\text{-}5\text{-}\eta^5\text{-}C_8H_{11})_2$ [16], $Ru(1\text{-}5\text{-}\eta^5\text{-}C_8H_{11})(1\text{-}3\text{-}\eta^3\text{:}5\text{-}6\text{-}\eta^2\text{-}C_6H_{11})$ [16], $[Ru(1\text{-}5\text{-}\eta^5\text{-}C_8H_{11})(PMe_2Ph)_3]^+[BPh_4]^-$ [17], and $[Ru(1\text{-}5\text{-}\eta^5\text{-}C_8H_{11})(\text{arene})]^+[PF_6]^-$ [18]. The ^{1}H–^{1}H COSY of **2a** revealed spin-correlated 11 protons suggesting the presence of a C_8H_{11} moiety. A quartet of triplets at 0.45 ppm is assigned as the aliphatic *endo*-proton H(7-*endo*) which is coupled to the three protons at 1.26 [H(7-*exo*)] and 2.06 ppm [H(6-*exo*) and H(8-*exo*)] with coincidentally the same coupling constant and two protons at 1.75 ppm [H(6-*endo*) and H(8-*endo*)]. The high-field shift of H(7-*endo*) is considered to be caused by the shielding effect of the η^5-cyclooctadienyl ligand. A triplet at 5.98 ppm is assigned to the central dienyl proton H(3) that is coupled to the neighboring dienyl protons [H(2) and H(4)] at 4.49 ppm. A broad peak at 3.05 ppm is coupled to both dienyl [H(2) and H(4)] and aliphatic protons [H(6) and H(8)] and is therefore assigned to the outer dienyl protons [H(1) and H(5)]. Two intensive broad singlets at 1.41 and 1.76 ppm are assigned as three PMe_3 ligands. A sharp singlet at 2.19 ppm, and two resonances in the aromatic region at 6.32 (t) and 6.75 (d) ppm are assignable to the ortho methyl, and para and meta protons, respectively. Detail analysis of the ^{1}H-NMR spectrum indicates that the relative integration ratios of the signals due to the aryloxo group always exceed the value expected, suggesting presence of accompanying 2,6-xylenol in **2a**. However, the signal due to the OH hydrogen was not observed. When one equivalent of 2,6-xylenol was added to **2a** at room temperature (r.t.), these signals of the aryloxo moieties completely merged into the unique set without significant broadening. These facts suggest the occurrence of rapid exchange reaction between 2,6-dimethylphenoxo anion and the associated 2,6-xylenol in NMR time scale. Treatments of **1**/PMe_3 with 2-allylphenol, phenol, *ortho*-cresol, 2-isopropylphenol, and 2-*tert*-butylphenol also yielded corresponding analogous (η^5-cyclooctadienyl)ruthenium(II) complexes $[Ru(\eta^5\text{-}C_8H_{11})(PMe_3)_3]^+[OAr]^-\cdot(HOAr)_n$ [Ar = $C_6H_3Me_2$-2,6 (**2a**), C_6H_4(2-$CH_2CH{=}CH_2$) (**2b**), C_6H_4{2-(*E*)-CH=CHMe} (**2c**), Ph (**2d**); C_6H_4Me-2 (**2e**); C_6H_4(2-$CHMe_2$) (**2f**), and C_6H_4(2-CMe_3) (**2g**)]. The coordination mode of the η^5-cyclooctadienyl ligand in these complexes was unambiguously confirmed by X-ray structure analysis of **2c** (Fig. 1 and Table 1).

The overall structure of **2c** is best regarded as three legged chair form with counter anion. Bond distances of Ru–C(1), Ru–C(2), Ru–C(3), Ru–C(4), and Ru–C(5) are in the range 2.17–2.31 Å, suggesting the C_8H_{11} moiety is coordinating to the Ru in an η^5-fashion. The aryloxo moiety is isomerized to (*E*)-propenylphenoxo group locating far from the ruthenium center and is associated with one molecule of (*E*)-2-propenylphenol, indicating the ionic character of **2c**. The orientation of two aryloxo moieties and the bond length between two oxygen atoms (2.46 Å) suggest hydrogen bonding between the aryloxo anion and 2-propenylphenol [19]. It is interesting to note that while the allyl moiety remained intact in the reaction of **1**/PMe_3 with 2-allylphenol giving **2b** at r.t., heating of the reaction mixture led to **2c**.

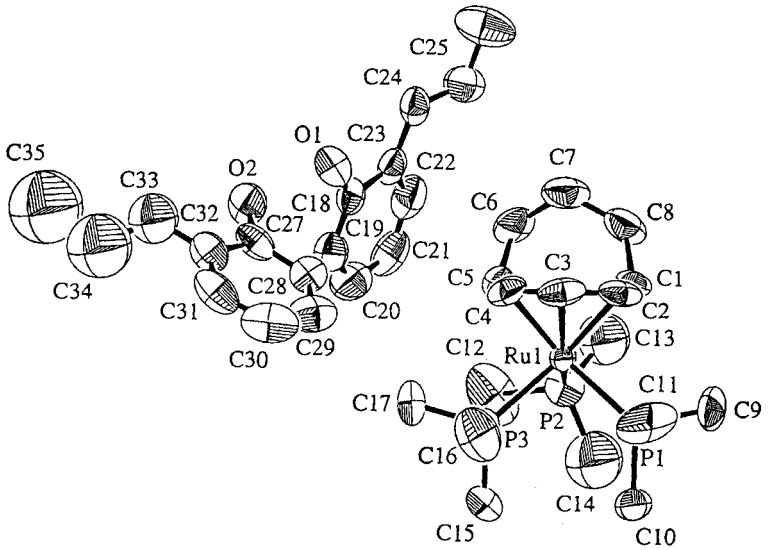
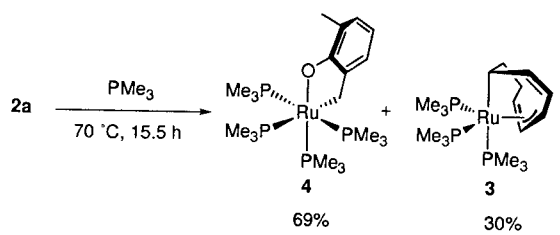


Fig. 1. Molecular structure of $[Ru(\eta^3\text{-}C_8H_{11})(PMe_3)_3]^+[OC_6H_4\{2\text{-}(E)\text{-}CH{=}CHMe\}]\cdot[HOC_6H_4\{2\text{-}(E)\text{-}CH{=}CHMe\}]$ (**2c**). Ellipsoids represent 50% probability. All hydrogen atoms are omitted for clarity.

Without exception, the reactions of **1**/PMe_3 with phenols quantitatively liberated 1,5-cyclooctadiene (1,5-COD) during the formation of **2**. Therefore the origin of the η^5-cyclooctadienyl group is considered to be the protonation of the 1,3,5-cyclooctatriene (1,3,5-COT) ligand in **1**. Actually, less protic alcohols or amine such as 2,6-dimethylcyclohexanol, *tert*-butyl alcohol or 2,6-dimethylaniline remained unreacted under these conditions, but protonation of **1** by acid such as HBF_4 is reported [17]. Phenols having bulky substituents at the *ortho* positions such as 2,6-diethylphenol, 2,6-di(isopropyl)phenol, or 2,6-di(*tert*-butyl)phenol also did not cause the protonation of the 1,3,5-COT ligand but gave *fac*-$Ru(6\text{-}\eta^1\text{:}1\text{-}3\text{-}\eta^3\text{-}C_8H_{10})(PMe_3)_3$ (**3**), which is independently prepared by the reaction of **1** with PMe_3 [20].

2.2. Reaction of $[Ru(\eta^5\text{-}C_8H_{11})(PMe_3)_3]^+[OAr]^-\cdot(HOAr)_n$ (2)

Treatment of $[Ru(\eta^5\text{-}C_8H_{11})(PMe_3)_3]^+[OC_6H_3Me_2\text{-}2,6]^-\cdot(HOC_6H_3Me_2\text{-}2,6)$ (**2a**) with PMe_3 at 70°C for 15.5 h resulted in sp^3 C–H bond cleavage of the *ortho* methyl group in the aryloxo anion giving an oxaruthenacycle complex *cis*-$\overline{Ru[OC_6H_3(2\text{-}CH_2)(6\text{-}Me)]}(PMe_3)_4$ (**4**) in 69% yield with concomitant formation of 1,3-COD and 2,6-xylenol. A small amount of **3** was also formed in the reaction (vide infra). The η^5-C_8H_{11} moiety is considered to act as the hydrogen acceptor for the C–H bond activation liberating 1,3-COD (Eq. (2)).



(2)

Complex **4** was characterized by NMR, IR and elemental analysis as well as chemical reactions. The ^{1}H-NMR spectrum of **4** shows a characteristic triplet of triplets at 2.68 ppm with 2H integration ratio due to the *ortho* methylene protons. This signal indicates that the *ortho* methylene group is directly bonded to Ru and is

Table 1
Selected bond lengths (Å) and angles (°) for **2c**

Ru(1)–P(1)	2.356(3)	Ru(1)–P(2)	2.317(3)
Ru(1)–P(3)	2.353(3)	Ru(1)–C(1)	2.31(1)
Ru(1)–C(2)	2.19(1)	Ru(1)–C(3)	2.23(1)
Ru(1)–C(4)	2.17(1)	Ru(1)–C(5)	2.29(1)
O(1)–O(2)	2.46(1)	C(1)–C(2)	1.38(2)
C(2)–C(3)	1.45(2)	C(3)–C(4)	1.43(2)
C(4)–C(5)	1.39(2)	C(5)–C(6)	1.52(2)
C(6)–C(7)	1.44(2)	C(7)–C(8)	1.56(2)
C(8)–C(1)	1.51(2)		
P(1)–Ru(1)–P(2)	96.9(1)	P(1)–Ru(1)–P(3)	91.9(1)
P(2)–Ru(1)–P(3)	93.1(1)	C(2)–C(1)–C(8)	125(1)
C(1)–C(2)–C(3)	127(1)	C(2)–C(3)–C(4)	123(1)
C(3)–C(4)–C(5)	129(1)	C(4)–C(5)–C(6)	123(1)
C(5)–C(6)–C(7)	118(1)	C(6)–C(7)–C(8)	112(1)
C(1)–C(8)–C(7)	114(1)		

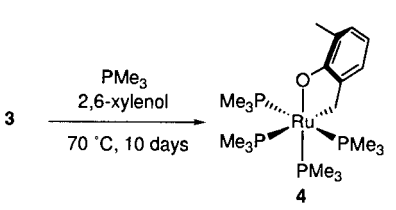
coupled to two magnetically equivalent *trans* P nuclei and two *cis* inequivalent P nuclei having coincidentally similar coupling constants. The *ortho* methyl group appears as a singlet at 2.53 ppm. The $^{31}P\{^{1}H\}$-NMR spectrum of **4** shows a typical AM_2X pattern at –13.8 (td, $J = 24$, 13 Hz, 1P), −0.96 (dd, $J = 32$, 24 Hz, 2P), and 10.7 ppm (td, $J = 32$, 13 Hz, 1P), suggesting that the PMe_3 ligands occupy the sites *trans* to each other and the residual two *cis* sites in an octahedral geometry. Two triplet of doublets at −13.8 and 10.7 ppm are assigned to the phosphorus nuclei *trans* to the methylene and aryloxo groups, respectively, reflecting the stronger *trans* influence by the alkyl ligand than the aryloxo ligand [15,21]. Protonolysis of **4** with HCl or HC≡CPh led to quantitative liberation of 2,6-xylenol supporting the oxaruthenacycle structure. Alternatively, **4** can also be derived from the reaction of **1**/PMe_3 with allyl 2,6-xylyl ether [14].

Similar C–H bond activation took place by heating of $[Ru(\eta^5\text{-}C_8H_{11})(PMe_3)_3]^+[OC_6H_4\{2\text{-}(E)\text{-}CH{=}CH\text{-}Me\}]\cdot[HOC_6H_4\{2\text{-}(E)\text{-}CH{=}CHMe\}]$ (**2c**) at 70°C giving a new oxaruthenacycle complex $Ru[OC_6H_4(2\text{-}\eta^3\text{-}C_3H_4)](PMe_3)_3$ (**5**), quantitatively. In this reaction 1,3,5-COT, 1,3-COD and 2-propylphenol were detected in 96, 7 and 101% yields, respectively. These results indicate that 2-propenylphenol acted as a hydrogen acceptor instead for this C–H bond cleavage. The X-ray structure of the PEt_3 analogue of **4** has been reported in a preliminary communication [14].

In contrast, reactions of **2d**–**g** with PMe_3 under similar conditions did not lead to the C–H bond activation of aryloxo group, but produced (hydrido)-(aryloxo)ruthenium(II) complexes *cis*-Ru(H)(OAr)-$(PMe_3)_4$ [Ar = Ph (**6a**), C_6H_4Me-2 (**6b**), $C_6H_4CHMe_2$-2 (**6c**), $C_6H_4CMe_3$-2 (**6d**)] with liberation of 1,3,5-COT.

2.3. Reaction of fac-Ru(6-η¹:1-3-η³-C_8H_{10})(PMe_3)$_3$ (3) with phenols

We previously reported formation of **3** by the reaction of **1** with PMe_3 in the absence of phenols [22]. Treatment of **3** with 2,6-xylenol in the presence of PMe_3 slowly but quantitatively gave **4** at 70°C for 10 days (Eq. (3)).



(3)

The NMR study of the reaction mixture revealed initial formation of **2a** followed by quantitative conversion to **4** after 326 h. No other intermediates were observed during the reaction (see Section 4). Similarly, treatments of **3** with 2-allylphenol and *ortho*-cresol also afforded **2c** and **2e**, respectively. These data suggest that **3** is also susceptible to protonation giving (η^5-cyclooctadienyl)ruthenium(II) (**2**). However, in all cases starting from **3**, the reaction giving **2** proceeded much slower compared to those from **1**/PMe_3 (see Section 4). These facts suggest that protonation of the COT ligand in **1**/PMe_3 is faster than protonolysis of the η^1:η^3-COT ligand in **3**.

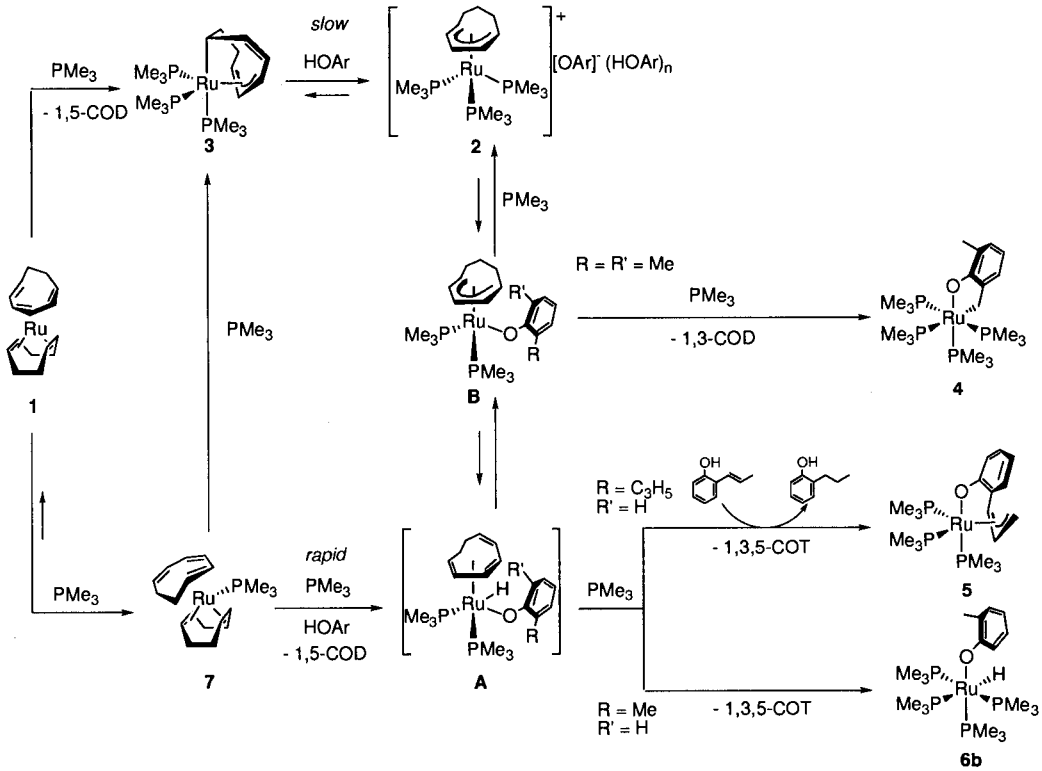
2.4. Possible mechanism for successive O–H and sp^3 C–H bond activation

By taking present results into account, a possible mechanism for these reactions is proposed as shown in Scheme 2.

As established previously, treatment of **1** with PMe_3 rapidly gives Ru(1-2-η^2;5-6-η^2-cod)(1-4-η^4-cot)(PMe_3) (**7**) [23] but the formation of **3** is basically very slow [22]. Both **3** and **7** give (η^5-cyclooctadienyl)ruthenium(II) **2** by the reaction with phenols, but the reaction of **3** is much slower than that of **7**. Therefore, **2** is probably formed directly from **7** rather than **3**. This process is regarded as a protonation since less protic alcohols such as 2,6-dimethylcyclohexanol remained unreacted. However, since bulky *ortho* substituents in phenols discouraged the formation of **2**, this process may involve prior protonation of phenols to Ru giving an intermediate such as **A**. This process is reasonable, since such a protonation process leading to the η^5-cyclooctadienyl intermediate **B** has been proposed by Tkachenko and Chaudret [17]. The aryloxo group in **B** can be displaced by PMe_3 to give a thermodynamically stable cationic complex **2**. When 2,6-xylenol bearing methyl groups at both *ortho*-positions is employed, one of the *ortho* methyl group is forced to approach to the ruthenium center in **B**, leading to sp^3 C–H bond cleavage to give **4** with liberation of 1,3-COD [24]. When the 1,3,5-COT ligand is simply liberated from **A**, (hydrido)(aryloxo)-ruthenium(II) complexes are formed. It should be noted that in these C–H bond activation, the presence of hydrogen acceptor is very important [25]. 1,3,5-COT acts as the hydrogen acceptor in the reaction of 2,6-xylenol, whereas in the reaction of 2-allylphenol, the reactant plays such role exclusively giving the hydrogenated product (2-propylphenol). Without exception no hydrogen evolution was observed in these reactions. It is also worthwhile to note that the sp^3 C–H bond cleavage is clearly subsequent to the protonation and thus occurs at a divalent ruthenium center in this system. Facile approach of the *ortho* substituent would induce the sp^3 C–H bond activation.

3. Conclusions

In summary, we have succeeded in successive O–H and sp^3 C–H bond activation of *ortho* substituted phe-



Scheme 2.

nol by a ruthenium(0) complex. Bennett reported a pioneering study on sp^2 C–H bond cleavage of ancillary phosphine ligand giving metallacycle complexes [26]. The present work demonstrates that sp^3 C–H bond of *ortho* substituted phenols can also be readily cleaved at ruthenium. This study provides fundamental aspects for sp^3 C–H bond activation of organic molecules by a low-valent ruthenium complex: (i) C–H bond should be approach to the low-valent metal center; (ii) selection of good hydrogen acceptor is also an important factor for the C–H bond cleavage; (iii) thermodynamic stability of the product may also be the driving force.

4. Experimental

4.1. General procedures

All manipulations were carried out under dry nitrogen using standard Schlenk and vacuum line techniques unless otherwise noted. Benzene, toluene, hexane, 1,4-dioxane and Et_2O were dried over anhydrous calcium chloride and then distilled from sodium benzophenone ketyl under nitrogen. Ru(1,5-cyclooctadiene)(1,3,5-cyclooctatriene) (**1**) was prepared according to the literature method except for the magnetic stirring instead of the ultrasonic irradiation during the reaction [16]. Ru(6-η^1:1-3-η^3-C_8H_{10})(PMe_3)$_3$ was prepared as reported previously [22,27]. PMe_3 was prepared from $P(OPh)_3$ with MeMgI. Phenols were purchased from Tokyo Chemical Industry or Aldrich and used as received. Deuterated solvents for use in NMR experiments were purchased from Kanto Chemical or Aldrich and dried with sodium wire for C_6D_6 and $CD_3C_6D_5$ and drierite for CD_3COCD_3, and were directly vacuum-transferred into NMR. NMR spectra were recorded on a JEOL LA-300 spectrometer (300.4 MHz for ^1H, 121.6 MHz for ^{31}P and 74.5 MHz for ^{13}C) with chemical shifts reported in ppm downfield from TMS for ^1H and ^{13}C, and from 85% H_3PO_4 in D_2O. IR spectra were recorded on a JASCO FTIR-410 spectrometer using KBr disks. Elemental analyses were carried out using a Perkin–Elmer 2400 series II CHN analyzer. Quantitative analyses of evolved gases were performed by GLC after collection of gases by using Toepler pump or by internal standard method by GLC.

4.2. Preparation of $[Ru(\eta^5\text{-}C_8H_{11})(PMe_3)_3]^+[OAr]^-\cdot(HOAr)_n$ (2)

As a typical example, preparation of **2a** by the reaction of **1**/PMe_3 with 2,6-xylenol at r.t. is described in detail. The other (η^5-cyclooctadienyl)ruthenium complexes **2b** and **2d–g** were prepared similarly and the yields and NMR data are shown below. Complex **2c** was also prepared analogously but the reaction was carried out at 70°C.

*4.2.1. [Ru(η⁵-C_8H_{11})(PMe_3)$_3$]⁺[$OC_6H_3Me_2$-2,6]⁻·($HOC_6H_3Me_2$-2,6) (**2a**)*

Complex **1** (332.8 mg, 1.055 mmol) was dissolved in dry hexane (3 ml) and PMe_3 (328 μl, 3.21 mmol) was added into the solution. Immediately after addition of 2,6-xylenol (515.7 mg, 4.221 mmol) into the solution at r.t., white powder was deposited. After stirring the suspension for 3 h, the solution was removed and the resulting white solid was washed with Et_2O (15 ml × 7) and then dried in vacuo to give **2a**. Yield, 322.5 mg (0.443 mmol, 42%). Complete purification of cationic complex **2a** was unsuccessful because of incorporation of 2,6-xylenol. Attempted recrystallization gave oily materials also including hydrogen bonded 2,6-xylenol. The amount of included 2,6-xylenol varied 1–2 mol per **2a**. Therefore, only spectroscopic data are shown below. ^{1}H-NMR (acetone-d_6): δ 0.45 (qt, J = 13.8, 2.7 Hz, 1H, *endo*-7-CH_2), 1.26 (m, 1H, *exo*-7-CH_2), 1.41 (m, 18Hz, PMe_3), 1.75 (br, 2H, *endo*-6- and *endo*-8-CH_2), 1.76 (m, 9H, PMe_3), 2.06 (br, 2H, *exo*-6- and *exo*-8-CH_2), 2.19 (s, 14.4H, $OC_6H_3Me_2$,), 3.05 (br, 2H, 1- and 5-CH), 4.49 (m, 2H, 2- and 4-CH), 5.98 (t, J = 6.3 Hz, 1H, 3-CH), 6.32 (t, J = 7.2 Hz, 2.8H, *para*-OC_6H_3), 6.75 (d, J = 7.2 Hz, 5.6H, *meta*-OC_6H_3). ^{31}P{^{1}H}-NMR (acetone-d_6): δ −5.95 (br, PMe$_3$).

*4.2.2. [Ru(η⁵-C_8H_{11})(PMe_3)$_3$]⁺[OC_6H_4-(2-$CH_2CH{=}CH_2$)]⁻·{HOC_6H_4(2-$CH_2CH{=}CH_2$)} (**2b**)*

Reaction of **1** (215.4 mg, 0.683 mmol)/PMe_3 (212 μl, 2.05 mmol) with 2-allylphenol (375 μl, 2.73 mmol) gave **2b**. Yield, 492.4 mg (0.617 mmol, 90%). ^{1}H-NMR (acetone-d_6): δ 0.45 (qt, 1H, J = 13.8, 2.7 Hz, 1H, *endo*-7-CH_2), 1.26 (m, 1H, *exo*-7-CH_2), 1.39 (br, 18 H, PMe_3), 1.67 (m, 2H, *endo*-6- and *endo*-8-CH_2), 1.75 (m, 9H, PMe_3), 2.11 (br, 2H, *exo*-6- and *exo*-8-CH_2), 3.05 (br, 2H, 1- and 5-CH), 3.39 (d, J = 6.3 Hz, 5.4 H, CH_2CH=CH$_2$), 4.47 (m, 2H, 2- and 4-CH), 4.90 (d, J = 9.9 Hz, 2.7 H, CH$_2$CH=CH_2), 5.02 (d, J = 16.5 Hz, 2.7 H, CH$_2$CH=CH_2), 5.97 (t, J = 6.5 Hz, 1H, 3-CH), 6.08 (ddt, J = 16.5, 9.9, 6.3 Hz, 2.7 H, CH$_2$CH=CH$_2$), 6.43 (t, J = 7.5 Hz, 2.7 H, OC_6H_4), 6.84 (t, J = 7.5 Hz, 2.7 H, OC_6H_4), 6.90 (d, J = 7.5 Hz, 2.7 H, OC_6H_4),6.98 (d, J = 7.5 Hz, 2.7 H, OC_6H_4). ^{31}P{^{1}H}-NMR (acetone-d_6): δ −5.99 (br, PMe$_3$).

*4.2.3. [Ru(η⁵-C_8H_{11})(PMe_3)$_3$]⁺[OC_6H_4{2-(E)-CH=CHMe}]⁻·[HOC_6H_4{2-(E)-CH=CHMe}] (**2c**)*

2-Allylphenol (260 μl, 1.99 mmol) was added to a benzene solution (3 ml) of **1** (310.9 mg, 0.986 mmol) with PMe_3 (390 μl, 3.01 mmol) and the reaction mixture was heated at 70°C for 3 days. Yield, 22.0 mg (0.0313 mmol, 3%). ^{1}H-NMR (acetone-d_6): δ 0.44 (qt, 1H, J = 13.8, 2.7 Hz, 1H, *endo*-7-CH_2), 1.29 (m, 1H, *exo*-7-CH_2), 1.37 (br, 18 H, PMe_3), 1.69 (m, 2H, *endo*-6- and *endo*-8-CH_2), 1.73 (m, 9H, PMe_3), 1.80 (dd, J = 6.3, 1.8 Hz, 6H, CH=CHMe), 2.10 (br, 2H, *exo*-6- and *exo*-8-CH_2), 3.01 (br, 2H, 1- and 5-CH), 4.47 (m, 2H, 2- and 4-CH), 5.95 (t, J = 6.4 Hz, 1H, 3-CH), 6.16 (dq, J = 16.1, 6.3 Hz, 2H, CH=CHMe), 6.31 (t, J = 7.5 Hz, 2H, OC_6H_4), 6.79 (td, J = 7.5, 1.8 Hz, 2H, OC_6H_4), 6.91 (dq, J = 16.1, 1.8 Hz, 2H,CH=CHMe), 6.92 (dd, J = 7.5, 1.8 Hz, 2H, OC_6H_4), 7.14 (dd, J = 7.5, 1.8 Hz, 2H, OC_6H_4). ^{31}P{^{1}H}-NMR (acetone-d_6): δ −5.99 (br, PMe$_3$). Anal. Calc. for $C_{35}H_{57}O_2P_3Ru$; C, 59.73; H, 8.16. Found: C, 60.55; H, 8.97%. The single crystals for X-ray analysis were obtained from the dilute benzene solution of **2c**.

*4.2.4. [Ru(η⁵-C_8H_{11})(PMe_3)$_3$]⁺[OPh]⁻·(HOPh) (**2d**)*

Reaction of **1** (112.7 mg, 0.357 mmol)/PMe_3 (125 μl, 1.07 mmol) with phenol (140.2 mg, 1.49 mmol) gave **2d**. Yield, 186.0 mg (0.277 mmol, 78%). ^{1}H-NMR (acetone-d_6): δ 0.45 (qt, 1H, J = 13.8, 2.7 Hz, 1H, *endo*-7-CH_2), 1.26 (m, 1H, *exo*-7-CH_2), 1.41 (br, 18 H, PMe_3), 1.71 (m, 2H, *endo*-6- and *endo*-8-CH_2), 1.76 (m, 9H, PMe_3), 2.11 (br, 2H, *exo*-6- and *exo*-8-CH_2), 3.06 (br, 2H, 1- and 5-CH), 4.49 (m, 2H, 2- and 4-CH), 5.99 (t, J = 6.3 Hz, 1H, 3-CH), 6.47 (t, J = 7.5 Hz, 2.5 H, *para*-OPh), 6.82 (t, J = 7.5 Hz, 5 H, *ortho*-OPh), 6.98 (t, J = 7.5 Hz, 5 H, *meta*-OPh). ^{31}P{^{1}H}-NMR (acetone-d_6): δ −5.94 (br, PMe$_3$).

*4.2.5. [Ru(η⁵-C_8H_{11})(PMe_3)$_3$]⁺[OC_6H_4Me-2]⁻·[HOC_6H_4(2-Me)] (**2e**)*

Reaction of **1** (149.8 mg, 0.475 mmol)/PMe_3 (170 μl, 1.46 mmol) with *ortho*-cresol (203.0 mg, 1.877 mmol) gave **2e**. Yield, 293.6 mg (0.416 mmol, 88%). ^{1}H-NMR (acetone-d_6): δ 0.45 (qt, 1H, J = 13.8, 2.7 Hz, 1H, *endo*-7-CH_2), 1.26 (m, 1H, *exo*-7-CH_2), 1.41 (br, 18 H, PMe_3), 1.71 (m, 2H, *endo*-6- and *endo*-8-CH_2), 1.76 (m, 9H, PMe_3), 2.11 (br, 2H, *exo*-6- and *exo*-8-CH_2), 2.15 (s, 4.5 H, OC_6H_4Me), 3.05 (br, 2H, 1- and 5-CH), 4.48 (m, 2H, 2- and 4-CH), 5.98 (t, J = 6.3 Hz, 1H, 3-CH), 6.40 (td, J = 7.6, 1.2 Hz, 2.5 H, *para*-OC_6H_4), 6.82 (dd, J = 7.6, 1.5 Hz, 2.5 H, *ortho*-OC_6H_4), 6.91 (dd, J = 7.6, 1.2 Hz, 2.5 H, *meta*-OC_6H_4), 6.93 (dd, J = 7.6, 1.5 Hz, 2H, *meta*-OC_6H_4). ^{31}P{^{1}H}-NMR (acetone-d_6): δ −5.96 (br, PMe$_3$).

*4.2.6. [Ru(η⁵-C_8H_{11})(PMe_3)$_3$]⁺[OC_6H_4(2-$CHMe_2$)]⁻·[HOC_6H_4(2-$CHMe_2$)] (**2f**)*

Reaction of **1** (211.9 mg, 0.672 mmol)/PMe_3 (240 μl, 2.06 mmol) with 2-isopropylphenol (360 μl, 2.68 mmol) gave **2f**. Yield, 361.8 mg (0.483 mmol, 72%). ^{1}H-NMR (acetone-d_6): δ 0.45 (qt, 1H, J = 13.8, 2.7 Hz, 1H, *endo*-7-CH_2), 1.17 (d, J = 7 Hz, 13.8 H, CHMe_2), 1.26 (m, 1H, *exo*-7-CH_2), 1.41 (br, 18 H, PMe_3), 1.72 (m, 2H, *endo*-6- and *endo*-8-CH_2), 1.76 (m, 9H, PMe_3), 2.11 (br, 2H, *exo*-6- and *exo*-8-CH_2), 3.06 (br, 2H, 1- and 5-CH), 3.20 (sep, J = 7 Hz, 2.3 H, CHMe$_2$), 4.50 (m, 2H, 2- and 4-CH), 6.00 (t, J = 6.3 Hz, 1H, 3-CH), 6.36 (td, J = 7.8, 1.2 Hz, 2.3 H, *para*-OC_6H_4), 6.76 (td,

$J = 7.8$, 1.8 Hz, 2.3 H, *ortho*-OC_6H_4), 6.93 (dd, $J = 7.8$, 1.8 Hz, 2.3 H, *meta*-OC_6H_4), 6.96 (dd, $J = 7.8$, 1.2 Hz, 2.3 H, *meta*-OC_6H_4). $^{31}P\{^1H\}$-NMR (acetone-d_6): δ −5.95 (br, PMe_3).

4.2.7. $[Ru(\eta^5\text{-}C_8H_{11})(PMe_3)_3]^+[OC_6H_4(2\text{-}CMe_3)]^-\cdot[HOC_6H_4(2\text{-}CMe_3)]$ (2g)

Reaction of **1** (189.0 mg, 0.599 mmol)/PMe_3 (180 μl, 1.54 mmol) with 2-*tert*-butylphenol (370 μl, 2.41 mmol) gave **2g**. Yield, 280.5 mg (0.340 mmol, 57%). ^{1}H-NMR (acetone-d_6): δ 0.45 (qt, 1H, $J = 13.5$, 2.7 Hz, 1H, *endo*-7-CH_2), 1.26 (m, 1H, *exo*-7-CH_2), 1.41 (br, 18 H, PMe_3), 1.43 (s, 23H, CMe_3), 1.72 (br, 2H, *endo*-6- and *endo*-8-CH_2), 1.76 (m, 9H, PMe_3), 2.11 (br, 2H, *exo*-6- and *exo*-8-CH_2), 3.05 (br, 2H, 1- and 5-CH), 4.49 (m, 2H, 2- and 4-CH), 5.98 (t, $J = 6.3$ Hz, 1H, 3-CH), 6.36 (td, $J = 7.7$, 1.3 Hz, 2.6H, *para*-OC_6H_4), 6.79 (td, $J =$ 7.8, 1.8 Hz, 2.6H, *ortho*-OC_6H_4), 6.97 (dd, $J = 7.7$, 1.3 Hz, 2.6H, *meta*-OC_6H_4), 7.02 (dd, $J = 7.7$, 18 Hz, 2.6H, *meta*-OC_6H_4). $^{31}P\{^1H\}$-NMR (acetone-d_6): δ -5.95 (br, PMe_3).

4.3. Preparation of *cis*-Ru[OC_6H_3(2-CH_2)(6-Me)]-(PMe_3)$_4$ (4)

PMe_3 (430 μl, 3.32 mmol) and 2,6-xylenol (134.4 mg, 1.10 mmol) were added into a benzene solution (5 ml) of **1** (346.5 mg, 1.10 mmol) in this order. The pale yellow solution was stirred at 70°C for 200 h. After removal of all volatile materials under reduced pressure, the resulting white solid was extracted with Et_2O (15 ml). The extract was evaporated to dryness and the resulting white powder was recrystallized from pentane at −30°C to yield white needles of *cis*-Ru[OC_6H_4(2-CH_2)(6-Me)](PMe_3)$_4$ (**4**). Yield, 143.5 mg (0.272 mmol, 25%). ^{1}H-NMR (C_6D_6): δ 0.90 (d, $J = 7.2$ Hz, 9H, *apical*-PMe_3), 1.00 (t, $J = 2.9$ Hz, 18H, *equatorial*-PMe_3), 1.17 (d, $J = 5.7$ Hz, 9H, *equatorial*-PMe_3), 2.53 (s, 3H, 6-*Me*), 2.68 (tt, $J = 14.3$, 3.5 Hz, 2H, 2-CH_2), 6.7–6.9, 7.1–7.2 and 7.4–7.5 (m, C_6H_3, overlapped with C_6D_5H). $^{31}P\{^1H\}$-NMR (C_6D_6): δ −13.8 (td, $J = 24$, 13 Hz, 1P, PMe_3 *trans* to CH_2), −0.96 (dd, $J = 32$, 24 Hz, 2P, mutually *trans* PMe_3), 10.7 (td, $J = 32$, 13 Hz, 1P, PMe_3 *trans* to O). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 17.8 (s, C_6H_3(6-*Me*)), 17.9 (td, $J = 11$, 3 Hz, PMe_3), 22.4 (d, $J = 14$ Hz, PMe_3), 23.2 (dq, $J = 54$, 10 Hz, Ru–CH_2–), 24.7 (d, $J = 24$ Hz, PMe_3), 112.2 (s, *para*-OC_6H_3), 124.5 (s, *ortho*-OC_6H_3), 126.0 (s, *meta*-OC_6H_3), 129.4 (s, *meta′*-OC_6H_3), 138.4 (s, 6-OC_6H_3), 173.2 (s, *ipso*-OC_6H_3); these assignments were confirmed by ^{13}C-^{1}H shift correlation spectroscopy. IR (KBr, cm^{-1}): 2969 (w, νCH), 2908 (m, νCH), 1575 (m), 1466 (m), 1451 (m), 1422 (s), 1404 (sh), 1299 (s), 1273 (s), 1061 (w), 938 (vs), 850 (m), 842 (m), 739 (m), 709 (m), 625 (m), 526 (w). Anal. Calc. for $C_{20}H_{44}OP_4Ru$: C, 45.71; H, 8.44. Found: C, 45.90; H, 8.50%.

4.4. Preparation of *fac*-Ru[OC_6H_4(2-η^3-C_3H_4)](PMe_3)$_3$ (5)

Complex **5** was prepared by the reaction of **3** (137.2 mg, 0.315 mmol) with 2-allylphenol (82 μl, 0.628 mmol) in benzene at 70°C for 65 h. Yield, 37.4 mg (0.0810 mmol, 26%). This complex was also prepared by the reaction of **1**/PMe_3 with 2-allylphenol in a similar way to **4**. ^{1}H-NMR (C_6D_6): δ 0.53 (d, $J = 8.1$ Hz, 9 H, PMe_3), 1.09 (d, $J = 7.2$ Hz, 9 H, PMe_3), 1.26 (d, $J = 7.5$ Hz, 9 H, PMe_3), 1.91 (dd, $J = 12.3$, 4.5 Hz, 1H, *anti*-C_3H_4), 2.95 (m, 1H, *syn*-C_3H_4), 4.20 (dq, $J = 12.3$, 7.5 Hz, 1H, *central*-C_3H_4), 4.89 (dt, $J = 7.5$, 3.6 Hz, 1H, *syn*-C_3H_4), 6.66 (t, $J = 7.3$ Hz, 1H, OC_6H_4), 6.85 (d, $J = 8.1$ Hz, 1H, OC_6H_4), 7.15 (ddd, $J = 8.1$, 7.3, 1.8 Hz, 1H, overlapped with residual benzene in C_6D_6), 7.24 (dd, $J = 7.3$, 1.8 Hz, 1H, OC_6H_4). $^{31}P\{^1H\}$-NMR (C_6D_6): δ -11.4 (t, $J = 25$ Hz, 1P, PMe_3), −0.49 (dd, $J = 25$, 16 Hz, 1P, PMe_3), −0.39 (dd, $J = 25$, 16 Hz, 1P, PMe_3). Anal. Calc. for $C_{18}H_{35}OP_3Ru$: C, 46.85; H, 7.64. Found: C, 46.75; H, 7.63%.

4.5. Preparation of *cis*-Ru(H)(OAr)(PMe_3)$_4$ (6)

As a typical example, preparation of **6a** is described. Complexes **6b**–**d** were also prepared in a similar way to **6a**.

4.5.1. *cis*-Ru(H)(OPh)(PMe_3)$_4$ (6a)

Complex **1** (417.2 mg, 1.32 mmol) and phenol (133.8 mg, 1.422 mmol) were placed into a Schlenk tube to which benzene (3 ml) was transferred under vacuum. Into the reaction mixture PMe_3 (690 μl, 5.33 mmol) was added by a hypodermic syringe to start the reaction and the mixture was stirred at 70°C for 160 h. All volatile matters were removed and recrystallization of the resulting white solid from hexane gave white microcrystals of **6a**. Yield, 100.0 mg (0.200 mmol, 15%). This complex was characterized by comparison with the literature data [15a].

4.5.2. *cis*-Ru(H)(OC_6H_4Me-2)(PMe_3)$_4$ (6b)

Reaction of **1** (191.8 mg, 0.6080 mmol)/PMe_3 (325 μl, 2.51 mmol) with *ortho*-cresol (86.3 mg, 0.798 mmol) gave **6b**. Yield, 76.2 mg (0.148 mmol, 24%). ^{1}H-NMR (C_6D_6): δ −7.55 (dq, $J = 102$, 27 Hz, 1H, Ru–*H*), 0.99 (d, $J = 7.2$ Hz, 9H, PMe_3), 1.15 (virtual t, $J = 2.8$ Hz, 18H,PMe_3), 1.17 (d, $J = 5.4$ Hz, 9H, PMe_3), 2.49 (s, 3H, 2-*Me*), 6.71 (t, $J = 6.6$ Hz, 1H, OC_6H_4), 7.38 (d, $J = 6.6$ Hz, 1H, OC_6H_4), 7.44 (t, $J = 8.1$ Hz, 1H, OC_6H_4), 7.65 (d, $J = 8.1$ Hz, 1H, OC_6H_4). $^{31}P\{^1H\}$-NMR (121.6 MHz, C_6D_6): δ −11.6 (td, $J = 27$, 16 Hz, 1P, PMe_3), 1.17 (dd, $J = 33$, 27 Hz, 2P, PMe_3), 15.2 (td, $J = 33$, 16 Hz, 1P, PMe_3). IR (KBr, cm^{-1}): 1858 (νRu–H). Anal. Calc. for $C_{19}H_{44}OP_4Ru$: C, 44.44; H, 8.64. Found: C, 45.13; 8.86%.

*4.5.3. cis-Ru(H)[OC_6H_4(2-$CHMe_2$)](PMe_3)$_4$ (**6c**)*

Reaction of **1** (115.2 mg, 0.365 mmol)/PMe_3 (170 μl, 1.46 mmol) with 2-isopropylphenol (59 μl, 0.44 mmol) gave **6e**. Yield, 29.6 mg (0.0544 mmol, 15%). ^{1}H-NMR (C_6D_6): δ −7.58 (dq, J = 103, 27 Hz, 1H, Ru–*H*), 0.98 (d, J = 7.2 Hz, 9H, P*Me*$_3$), 1.16 (virtual t, J = 3.0 Hz, 18H, P*Me*$_3$), 1.18 (d, J = 5.4 Hz, 9H, P*Me*$_3$), 1.49 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 3.80 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 6.77 (t, J = 7.7 Hz, 1H, OC_6H_4), 7.39 (d, J = 7.7 Hz, 1H, OC_6H_4), 7.40 (t, J = 7.7 Hz, 1H, OC_6H_4), 7.70 (d, J = 7.7 Hz, 1H, OC_6H_4). ^{31}P{^{1}H}-NMR (C_6D_6): δ −12.5 (td, J = 27, 17 Hz, 1P, *P*Me$_3$), 1.34 (dd, J = 33, 27 Hz, 2P, *P*Me$_3$), 15.3 (td, J = 33, 17 Hz, 1P, *P*Me$_3$). IR (KBr, cm^{-1}): 1873 (νRu–H). Anal. Calc. for $C_{21}H_{48}OP_4Ru$: C, 46.57; H, 8.93. Found: C, 46.39; H, 8.69%.

*4.6. Reaction of [Ru(η^5-C_8H_{11})(PMe_3)$_3$]$^+$[OAr](HOAr)$_n$ (**2**) with PMe_3*

The following reactions were carried out in an NMR tube in benzene-d_6 at 70°C in the presence of an internal standard (1,4-dioxane) and the yields of products are described below.

Reaction of [Ru(η^5-C_8H_{11})(PMe_3)$_3$]$^+$[$OC_6H_3Me_2$-2,6]$^-$·($HOC_6H_3Me_2$-2,6) (**2a**) (4.7 mg, 0.0065 mmol) with PMe_3 (1.0 μl, 0.0097 mmol) at 70°C for 15.5 h gave Ru[OC_6H_3(2-CH_2)(6-Me)](PMe_3)$_4$ (**4**) (69%), 1,3-COD (69%), 2,6-xylenol (293%) and **3** (30%).

Heating of [Ru(η^5-C_8H_{11})(PMe_3)$_3$]$^+$[OC_6H_4{2-(*E*)-CH=CHMe}]$^-$·[H OC_6H_4{2-(*E*)-CH=CHMe}] (**2c**) (3.0 mg, 0.0043 mmol) at 70°C for 17 h gave Ru[OC_6H_4(2-η^3-C_3H_4)](PMe_3)$_3$ (**5**) (100%), 1,3-COD (7%), 2-propylphenol (101%), and 1,3,5-COT (96%).

Reaction of [Ru(η^5-C_8H_{11})(PMe_3)$_3$]$^+$[OC_6H_4Me-2]$^-$·(HOC_6H_4Me-2) (**2e**) (8.9 mg, 0.012 mmol) with PMe_3 (4.0 μl, 0.039 mmol) at 70°C for 10 h: *cis*-Ru(H)(OC_6H_4Me-2)(PMe_3)$_4$ (**6b**) (71%), *ortho*-cresol (210%), and 1,3,5-COT (46%).

*4.7. Reaction of fac-Ru(6-η^1:1-3-η^3-C_8H_{10})(PMe_3)$_3$ (**3**) with phenols*

*4.7.1. Reaction of **3** with 2,6-xylenol*

A mixture of **3** (8.6 mg, 0.020 mmol) and 2,6-dimethylphenol (2.8 mg, 0.023 mmol) were dissolved in C_6D_6 (600 μl). After addition of PMe_3 (5.0 μl, 0.05 mmol) by hypodermic syringe, the reaction mixture was heated at 70°C for 10 days to give **4** (91%) and 1,3-COD (90%).

*4.7.2. Reaction of **3** with 2-allylphenol*

Reaction of **3** (15.1 mg, 0.0347 mmol) with 2-allylphenol (18 μl. 0.151 mmol) after 215 h in C_6D_6 (600 μl) at 70°C gave **5** (54%), 1,3,5-COT (38%), 2-propylphenol (48%), and 1,3-COD (9%).

*4.7.3. Reaction of **3** with ortho-cresol*

Complex **3** (167.7 mg, 0.385 mmol) and *ortho*-cresol (71.7 mg, 0.663 mmol) were dissolved in benzene (3 ml) and PMe_3 (62 μl, 0.60 mmol) was added into the solution. The reaction mixture was stirred at 70°C for 72 h. After removal of all volatile matters, resulting yellow oil was crystallized from a mixture of THF (1 ml) and hexane (1 ml) to give white cubes of **6b**. Yield, 57.3 mg (0.112 mmol, 29%).

*4.8. Acidolysis of **4** by HCl*

Complex **4** (18.3 mg, 0.035 mmol) was placed in an NMR tube and benzene-d_6 (600 μl) was transferred into the NMR tube under vacuum. Into the benzene-d_6 solution of **4** were added 1,4-dioxane (2.0 μl, 0.023 mmol) as an internal standard (1,4-dioxane) and 6 M HCl (20 μl, 0.13 mmol). The ^{1}H-NMR showed formation of 2,6-xylenol (93%, 0.028 mmol).

*4.9. Protonolysis of **4** by phenylacetylene*

Complex **4** (9.1 mg, 0.017 mmol) was placed in an NMR tube and benzene-d_6 (600 μl) was transferred into the NMR tube under vacuum. Into the solution were added 1,4-dioxane (2.0 μl, 0.023 mmol) as an internal standard and phenylacetylene (6.0 μl, 0.055 mmol) by a hypodermic syringe. The ^{1}H-NMR spectrum showed formation of 2,6-xylenol (100%, 0.017 mmol).

*4.10. X-ray structure analysis of **2c***

Complex **3** (97.3 mg, 0.223 mmol) was dissolved into a benzene solution (2 ml) and then 2-allylphenol (30 μl, 0.23 mmol) was added into the solution. The reaction mixture was stirred at 70°C for 65 h. All volatile materials were removed from the mixture to give a light yellow solid. Recrystallization of the solid from cold Et_2O (ca. 3 ml) gave a white precipitate, while complex **5** was obtained from the mother liquor in 11% yield (11.3 mg, 0.0245 mmol). Recrystallization the white precipitate from cold benzene gave clear light yellow cubes of **2c**. Yield, 76.2 mg (0.108 mmol, 48%).

A Rigaku AFC-5R diffractometer with graphite-monochromated Mo–K_α radiation (λ = 0.71069 Å) was used for data collection. A selected crystal of **2c** was mounted in glass capillaries (GLAS, 0.7 mmf) under argon atmosphere. The collected data were solved by Patterson methods, and refined by a full-matrix least-square procedure using TEXSAN programs [28]. The reflections with $|F_o| > 3\sigma|F_o|$ were used in the refinements. All non-hydrogen atoms except C(13) and C(18)–C(21) were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and were not refined. Crystallographic data for **2c** is as follows: light yellow cube with crystal

dimensions of $0.92 \times 0.45 \times 0.30$ mm; $C_{26}H_{46}OP_3Ru \cdot C_9H_{11}O$; $a = 19.423(6)$, $b = 23.974(8)$, $c = 16.099(8)$ Å, $V = 7496(4)$ Å^3; Mo–K_α : $\lambda = 0.71069$ Å; orthorhombic; *Pbca* (no. 61); $Z = 8$; Rigaku AFC-5R diffractometer; collection method: ω–2θ ; reflections collected: 8428; 2θ limit = 54.9°; empirical ϕ-scan absorption correction was applied; $R = 0.073$; $R_w = 0.097$.

5. Supplementary material

Tables of complete crystallographic data, bond lengths, bond angles, anisotropic thermal parameters, and final atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre, CCDC 139412. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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