Synthesis, Structure, and Reactivity of Novel Ruthenium(II) Phenolate Complexes

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Reaction of Ru(η^6-cot)(dmfm)$_2$ (**1**) [cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate] with phenol was investigated. At 110 °C, a novel ruthenium(II) phenolate complex, Ru(η^5-C_6H_5O)(η^5-C_8H_{11}) (**2**), was obtained by the reaction of **1** with phenol in an isolated yield of 52% (74% by NMR). When the reaction was carried out at 130 °C, further dehydrogenative ring-closure in an η^5-cyclooctadienyl ligand occurred to give Ru(η^5-C_6H_5O)(η^5-C_8H_9) (**3**) in an isolated yield of 61% (76% by NMR). For both complexes, the η^5-oxocyclohexadienyl bonding mode of a phenoxo ligand was clearly shown by X-ray crystallography and DFT calculation. Complex **2** was smoothly transformed into complex **3** in the presence of dmfm at 130 °C for 3 h. Selective *O*-methylation of an η^5-oxocyclohexadienyl ligand in complex **3** proceeded with methyl *p*-toluenesulfonate to give a novel cationic ruthenium(II) complex, [Ru(η^6-C_6H_5OMe)(η^5-C_8H_9)]$^+$OTs$^-$ (**4**), in an isolated yield of 74%.

Introduction

Phenols form an interesting class of arenes and are attractive in coordination chemistry.[1] The most obvious potential anionic π-arene ligand is the phenoxide ion, $C_6H_5O^-$. Whether this ion will bind to the metal through oxygen as in well-known phenoxo complexes[2] or will be π-bonded as in oxocyclohexadienyl complexes[3] depends on the nature of the metal and its ligands. As for the ruthenium, in a pioneering study by Wilkinson and coworkers, the first ruthenium(II) phenolate complex, RuH(C_6H_5O)(PPh_3)$_2$, was synthesized, and its structure was discussed by the spectroscopic analyses in 1976.[4]

On the other hand, in a continuation of our study of Ru(η^6-cot)(dmfm)$_2$ (**1**)[5] [cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate], we recently showed that a variety of novel zerovalent ruthenium complexes such as mono- and diphosphine,[6] aqua,[7] *p*-quinone,[8] amine,[9a] poly(pyridyl),[9b,c] and η^6-arene complexes[10] were prepared in high yields with high selectivity using complex **1** as a versatile starting material.

Herein, we report the synthesis of novel ruthenium(II) phenolate complexes, in which a phenoxide ligand has an η^5-oxocyclohexadienyl mode, by the reaction of complex **1** with phenol. In the present reaction, forced deprotonation of phenol was not needed, and a cot ligand smoothly inserted into a hydrido−ruthenium bond, which was generated by oxidative addition of phenol to **1**, to give an η^5-cyclooctadienyl ligand. The structures of new ruthenium(II) phenolate complexes are confirmed by IR, NMR, and X-ray analyses as well as DFT calculation.

Results and Discussion

Reaction of Ru(η^6-cot)(dmfm)$_2$ (**1**) (0.50 mmol) and an excess amount of phenol (3.0 g) was carried out at 110

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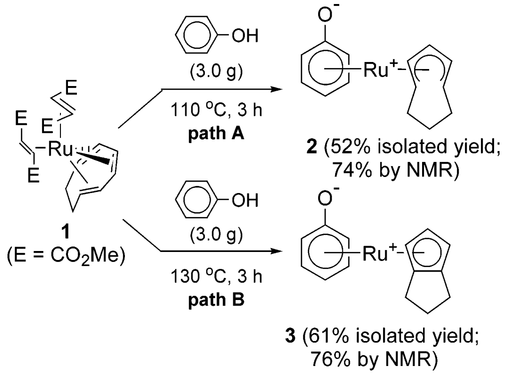
Scheme 1. Synthesis of Novel Ru(II) Phenolate Complexes



°C for 3 h under an argon atmosphere. After removal of unreacted phenol at 100 °C under vacuum, the yellow residue was washed with pentane and diethyl ether and vacuum-dried to give pale yellow crystals of a novel ruthenium(II) phenolate complex, Ru(η^5-C_6H_5O)(η^5-C_8H_{11})·C_6H_5OH (**2**·C_6H_5OH) [C_8H_{11} = cyclooctadienyl], in an isolated yield of 52% (74% by NMR) (Scheme 1, path A). When the same reaction was carried out at elevated temperature (at 130 °C), dehydrogenative ring-closure of an η^5-cyclooctadienyl ligand to an η^5-pentalenyl ligand occurred to give Ru(η^5-C_6H_5O)(η^5-C_8H_9)·2C_6H_5OH (**3**·2C_6H_5OH) [C_8H_9 = pentalenyl], in an isolated yield of 61% (76% by NMR) (Scheme 1, path B). The reaction using phenol as a solvent and a reagent gave the best result. Concomitant use of other solvents such as toluene, THF, and 1,2-dichloroethane with phenol completely suppressed the reaction, and complex **1** was almost recovered without the formation of **2** and **3**. In addition, a zerovalent ruthenium complex, Ru(η^4-cod)(η^6-cot) [cod = 1,5-cyclooctadiene], which is the starting material for the synthesis of complex **1**, also gave **2** and **3** by the reaction of phenol under the same reaction conditions; however, the yields of **2** and **3** were quite low (ca. 10% each).

Single crystals of complexes **2** and **3** suitable for X-ray crystallographic analysis were obtained by slow diffusion of pentane into CH_2Cl_2 and/or $CHCl_3$ solutions of **2** and **3**, respectively. Low-temperature X-ray diffraction studies of **2** and **3** clearly showed the η^5-oxocyclohexadienyl bonding mode of a phenoxo ligand (Figures 1 and 2). The crystal data and the experimental details for **2** and **3** are summarized in Table 1, and lists of the selected bond distances and angles for both complexes are provided in Tables 2 and 3.

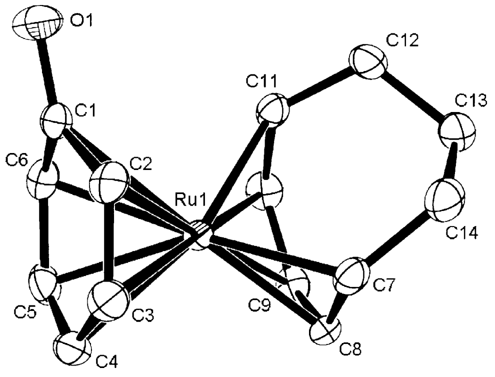


Figure 1. Molecular structure of **2**·PhOH with thermal ellipsoids drawn at the 50% probability level. PhOH molecule and hydrogen atoms are omitted for clarity.

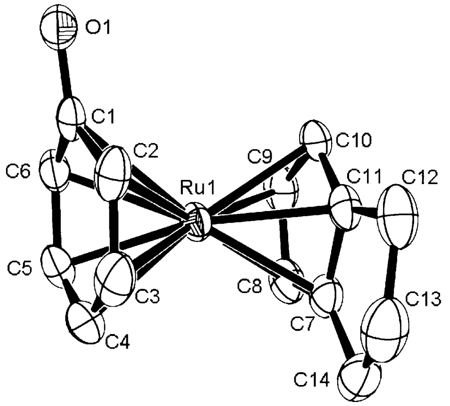


Figure 2. Molecular structure of **3**·2PhOH with thermal ellipsoids drawn at the 50% probability level. PhOH molecule and hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Data for the Structurally Analyzed Complexes 2·PhOH, 3·2PhOH, and 4

	2·PhOH	**3**·2PhOH	**4**
empirical formula	$C_{20}H_{22}O_2Ru$	$C_{26}H_{26}O_3Ru$	$C_{22}H_{24}O_4RuS$
fw	395.46	487.56	485.56
cryst color	colorless	yellow	colorless
habit	needle	block	needle
cryst size (mm)	0.30 × 0.05 × 0.03	0.30 × 0.30 × 0.10	0.30 × 0.10 × 0.05
cryst syst	monoclinic	monoclinic	monoclinic
space group	*P*21/*c* (#14)	*P*21/*n* (#14)	*P*21/*n* (#14)
a (Å)	6.5555(3)	7.1423(3)	6.8703(3)
b (Å)	14.5649(6)	15.720(1)	15.587(1)
c (Å)	14.6469(6)	19.050(1)	18.2670(9)
α (deg)	90	90	90
β (deg)	97.350(1)	94.864(2)	93.9791(9)
γ (deg)	90	90	90
V (Å^3)	1387.0(1)	2131.2(2)	1951.4(2)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.894	1.519	1.653
μ(Mo Kα) (cm^{-1})	11.39	7.61	9.369
λ (Å)	0.71070	0.71070	0.71070
T (°C)	−100	−100	−130
scan mode	ω−2θ	ω−2θ	ω−2θ
scan width (deg)	0.9327−1.0431	1.000−1.000	0.8969−1.0721
scan speed (deg min^{-1})	5.0	5.0	5.0
2θ_{max} (deg)	55.0	55.0	54.9
no. of measd reflns[a]	12 544	17 486	17 005
no. of obsd reflns[b]	2320	3746	2180
R^c (%)	3.4	3.1	3.5
$R_w{}^c$ (%)	4.5	3.5	3.7
GOF[d]	0.847	1.107	1.072

[a] Total. [b] $I > 3.00\sigma(I)$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$. [d] Goodness of fit.

The average bond distances between Ru and the five olefinic carbons of a phenoxo ligand (Ru−C2, Ru−C3, Ru−C4, Ru−C5, and Ru−C6) in **2** and **3** are 2.23 and 2.21 Å, respectively. On the other hand, the bond lengths between Ru and the carbon bearing the oxygen atom, i.e., Ru−C1 (2.471(4) and 2.414(2) Å), are longer than the average distance by ca. 0.2 Å. In addition, the bond distances of C1−O1 in complexes **2** and **3** are 1.256(5) and 1.283(3) Å, respectively, which

Table 2. Selected Bond Distances (Å) and Angles (deg) of Complexes 2 and 3

	2·PhOH	**3**·2PhOH
Bond Distances		
Ru−C1	2.471(4)	2.414(2)
Ru−C2	2.216(4)	2.237(3)
Ru−C3	2.209(5)	2.204(3)
Ru−C4	2.255(5)	2.198(3)
Ru−C5	2.219(4)	2.193(2)
Ru−C6	2.248(4)	2.240(2)
Ru−C7	2.184(4)	2.184(2)
Ru−C8	2.145(4)	2.196(2)
Ru−C9	2.193(4)	2.182(3)
Ru−C10	2.150(5)	2.193(2)
Ru−C11	2.168(4)	2.179(2)
Ru−C12	3.277(5)	3.272(3)
Ru−C13	3.695(5)	3.605(4)
Ru−C14	3.310(5)	3.272(3)
C1−O1	1.256(5)	1.283(3)
Bond Angles		
Ru−C1−O1	137.8(3)	135.7(2)
O1−C1−C2	124.1(4)	122.7(2)
O1−C1−C6	122.0(4)	122.2(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) of Complex 4

Bond Distances			
Ru−C1	2.233(4)	Ru−C10	2.167(5)
Ru−C2	2.226(4)	Ru−C11	2.188(5)
Ru−C3	2.214(5)	Ru−C12	2.202(4)
Ru−C4	2.204(5)	Ru−C13	3.301(4)
Ru−C5	2.194(5)	Ru−C14	3.591(4)
Ru−C6	2.216(4)	Ru−C15	3.282(5)
Ru−C8	2.190(4)	C1−O1	1.357(6)
Ru−C9	2.175(4)	O1 −C7	1.425(7)
Bond Angles			
Ru−C1−O1	131.1(3)	O1−C1−C2	115.6(4)
C1−O1−C7	117.8(4)	O1−C1−C6	123.6(4)

are a typical length in transition metal quinone complexes.

Simplified side views of complexes **2** and **3** are shown in Figure 3. The dihedral angles between the plane of five olefinic carbons, C2−C6, and the planes that include C1, C2, and C6 are 17.8° and 11.1°, respectively. However, these values are small compared to those in other η^5-oxocyclohexadienyl complexes. Thus, we expect that there should be a small contribution of the η^6-phenoxide bonding mode in the structure (Scheme 2). The hydrogen atoms in the η^5-oxocyclohexadienyl ligands of **2** and **3** are located at slightly leaned positions toward the ruthenium center, and the η^5-oxocyclohexadienyl ligands are shaped like an umbrella, which are consistent with the DFT optimized structures.

Further information of the phenoxo ligand arises from the position of ν(C−O) in the complexes. In the IR spectra, both **2** and **3** showed strong ν(C−O) absorption bands at 1536 and 1529 cm^{-1}, respectively. In comparison, ν(C−O) for complexes of *O*-bonded phenoxide usually occur in the region of 1200−1300 cm^{-1}. This indicates that the C−O bond of the phenoxo moiety has substantial double-bond character, and this is again best explained in terms of a large contribution from the η^5-oxocyclohexadienyl bonding mode in Scheme 2. In addition, ^{13}C NMR spectra of **2** and **3** showed the carbonyl carbons of an η^5-oxocyclohexadienyl ligand at 156.78 and 150.16 ppm, respectively.

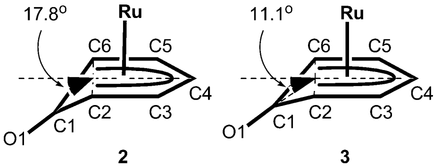
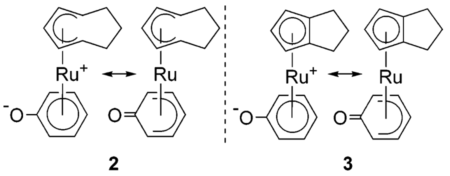
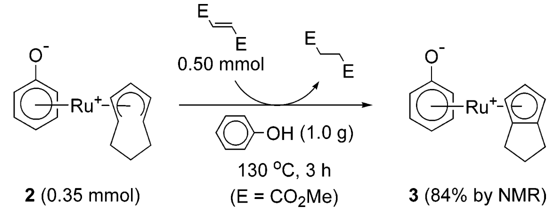


Figure 3. Simplified side views of **2** and **3**. Hydrogen atoms and η^5-cyclooctadienyl and η^5-pentalenyl ligands are omitted for clarity.

Scheme 2. Resonance Hybrids for π-Complexing of Phenoxo Group



Scheme 3. Ring-Closing Transformation of 2 to 3 in the Presence of Dimethyl Fumarate and Phenol



Complexes **2** and **3** crystallized with additional molecules of phenol. The obvious and strong hydrogen bonding between the O-H hydrogen in phenol molecules and the oxygen of the η^5-oxocyclohexadienyl ligands plays an important part in stabilization of complexes **2** and **3** as well as controlling the reactivity of the η^5-oxocyclohexadienyl ligands in **2** and **3**.

Since complex **3** was considered to be generated from **1** via **2**, transformation of complex **2** to **3** was investigated. Actually, when complex **2** was treated with phenol in the presence of dmfm at 130 °C for 3 h, complex **3** was obtained in an NMR yield of 84% (Scheme 3).

Without dmfm, the yield of **3** was drastically decreased. From careful analysis of the reaction mixture obtained from Scheme 3, dimethyl succinate, which would be formed by hydrogenation of dmfm, was detected by the ^{1}H NMR spectrum. Synthesis of a pentalenyl ruthenium complex by gas phase reaction of cyclooctadienyl ruthenium complex[11] or by the reaction of cyclododeca-1,5,9-triene[12] and cyclooctatetraene[13] with bis(germyl)ruthenium and osmium complexes has already been reported. However, the reaction conditions are sometimes severe and the yields of the product complexes were not satisfactory. Moreover, the mechanism of the ring contraction of cyclododeca-1,5,9-triene is not yet clear.

The structures and the electronic characters of the complexes were optimized by DFT calculation at the

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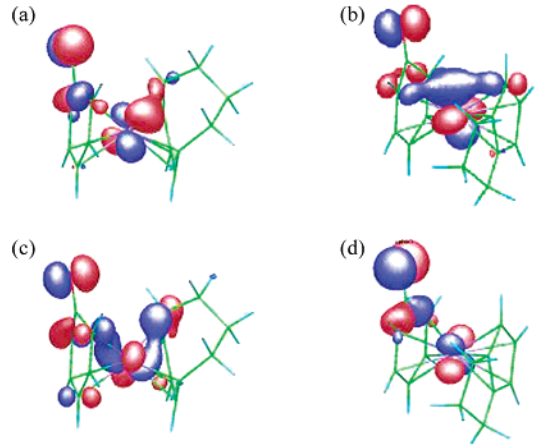
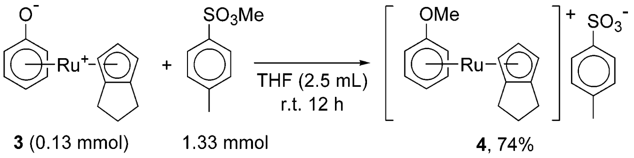


Figure 4. Drawings of HOMO of (a) **2** and (b) **3**, and those of HOMO-1 of (c) **2** and (d) **3** estimated by DFT calculation at the B3LYP/SDD + 6-31G(d,p) level.

Scheme 4. Synthesis of 4 by *O*-Methylation of 3 with Methyl *p*-Toluenesulfonate



B3LYP/SDD + 6-31G(d,p) level. The intramolecular dimensions of the theoretically optimized structures of **2** and **3** are generally comparable to those found in the solid state structure. For example, the bond distances between Ru1 and C2−C6 (average) and C1−O1 are 2.28 and 1.23 Å for **2** and 2.24 and 1.23 Å for **3**, respectively, very close to the values found in the solid state structures. The dihedral angles between the plane of C2−C6 and that of C1, C2, and C6 are 19.8° for **2** and 20.7° for **3**. This indicates that the DFT study slightly underestimates the contribution of the η^6-phenoxide bonding mode.

The shapes of the HOMOs and sub-HOMOs of **2** and **3** indicate the presence of antibonding repulsions, which would destabilize the π component of the C1−O1 bonds to some extent, as shown in Figure 4. Such destabilization would increase the nucleophilic character of O1 atoms. The DFT calculation also revealed that the transformation of the complex **2** to **3** is thermodynamically favored by 34.1 kcal mol^{-1} based on electronic and zero-point energies when the two hydrogen atoms are removed by hydrogenation of dmfm to dimethyl succinate.

Further reactivity of complex **3** was shown by the reaction with methyl *p*-toluenesulfonate. The oxygen atom of the η^5-oxocyclohexadienyl ligand is still nucleophilic (vide supra), and selective *O*-methylation of this ligand gave a novel cationic ruthenium(II) complex, [Ru(η^6-C_6H_5OMe)(η^5-C_8H_9)]$^+$OTs$^-$ (**4**), in an isolated yield of 74%. Single crystals of complex **4** suitable for X-ray crystallographic analysis were also obtained by slow diffusion of pentane into $CHCl_3$ solutions of **4** (Scheme 4 and Figure 5). As can be readily seen from Figure 5, η^6-coordination of the C_6H_5OMe ligand is apparent and the six carbons (C1−C6) of the C_6H_5 moiety are almost in one plane. The bond length of C1−Ru1 (2.233(4) Å) was shorter than those in **2** (2.471(4) Å) and **3** (2.414(2) Å), while the bond length of C1−O1 (1.357(6) Å) was longer than those in **2** (1.256(5) Å) and **3** (1.283(3) Å) (see Tables 2 and 3). In addition, no phenol molecule was observed in the crystal structure of **4**.

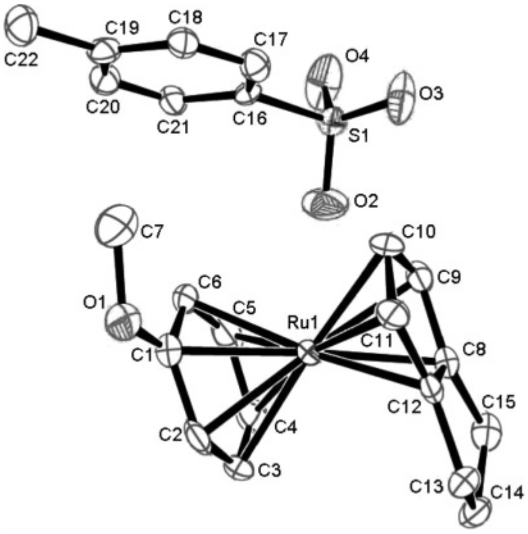
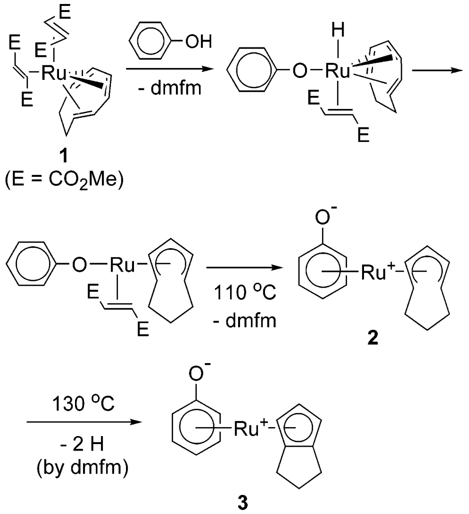


Figure 5. Molecular structure of **4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 5. Plausible Mechanism for the Formation of 2 and 3 from 1



Considering the results described above, the most plausible pathway for the formation of **2** and **3** from **1** is illustrated in Scheme 5. We now believe that the initial step of the present reaction is oxidative addition of phenol to **1**, which gives a (hydrido)(phenoxo)ruthenium complex with liberation of one dmfm ligand. Insertion of a 1,3,5-cyclooctatriene ligand into a hydrido−ruthenium bond and the subsequent σ−π rearrangement of the phenoxo ligand with dissociation of another dmfm ligand would give the novel ruthenium(II) phenolate complex **2** in high yield with high selectivity. Hence, at 130 °C, further dehydrogenative ring-closure of an η^5-cyclooctadienyl ligand in **2** occurs to give pentalenyl complex **3**.

Conclusion

In conclusion, novel ruthenium(II) phenolate complexes, **2** and **3**, were synthesized by simple and selective oxidative transformation of **1** with phenol. The phenoxo ligand can be considered to be bound as an η^6-phenoxo or more realistically as an η^5-oxocyclohexadienyl ligand, even though the oxygen atom showed high nucleophilicity. Our current interest is now focusing on the application of these complexes to new catalytic reactions such as *anti*-Markovnikov addition of phenol and/or alcohols to terminal alkenes.

Experimental Section

General Methods. All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed using standard Schlenk techniques and in dried and thoroughly deoxygenated solvents. Unless otherwise stated, all reagents were used as received from commercial suppliers. Ru(η^6-cot)(dmfm)$_2$[5] and Ru(η^4-cod)(η^6-cot)[14] were prepared as described in the literature. The ^{1}H NMR spectra were recorded at 400 MHz, while ^{13}C NMR spectra were recorded at 100 MHz with a JEOL EX400 spectrometer at 25 °C. Samples were analyzed in $CDCl_3$ or CD_2Cl_2, and the chemical shifts are given in ppm relative to Me_4Si. Dibenzil was used as an internal standard in order to determine the NMR yields of **2** and **3**. IR spectra were obtained on a Nicolet Impact 410 spectrometer. GC/MS analyses were performed using a Shimadzu QP5000 mass spectrometer connected with a Shimadzu GC-17A gas chromatograph [column: J & W Scientific capillary column DB-1, 0.25 mm i.d. × 25 m (film thickness 0.25 μm)]. Melting points were measured on a Yanagimoto micro melting point apparatus under an atmosphere of argon and are uncorrected. High-resolution mass spectra (FAB) were recorded on a JEOL SX102A spectrometer with *m*-nitrobenzyl alcohol (*m*-NBA) as a matrix. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Synthesis of Ru(η^5-C_6H_5O)(η^5-C_8H_{11})·C_6H_5OH (2·C_6H_5OH). A mixture of Ru(η^6-cot)(dmfm)$_2$ (**1**) (250 mg, 0.50 mmol) and phenol (3.0 g) was placed in a two-necked 50 mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser under a flow of argon. The mixture was heated at 110 °C for 3 h with stirring. Then, the reaction mixture was cooled, and removal of excess phenol under vacuum at 100 °C led to a colorless solid of complex **2**·C_6H_5OH, which was washed with pentane and diethyl ether (ca.. 5 mL each) and vacuum-dried (103 mg, 52%). Crystals suitable for X-ray analysis were grown by layering pentane on a concentrated CH_2Cl_2 solution at room temperature. Mp: 122.8−125.2 °C (dec). IR (KBr disk): 1575, 1527, 1473 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.03 (tq, 1H, CH*H* of C_8H_{11}, *J* = 2.7, 8.3 Hz), 1.17−1.24 (m, 1H, C*H*H of C_8H_{11}), 1.41 (dt, 1H, CH*H* of C_8H_{11}, *J* = 2.9, 7.3 Hz), 1.46 (dt, 1H, C*H*H of C_8H_{11}, *J* = 2.9, 7.3 Hz), 1.85−1.92 (m, 2H, CH_2 of C_8H_{11}), 3.84 (dt, 2H, CH of C_8H_{11}, *J* = 3.4, 4.4 Hz), 4.47 (t, 2H, CH of C_8H_{11}, *J* = 7.3 Hz), 5.24 (t, 1H, CH of C_8H_{11}, *J* = 5.4 Hz), 5.40 (d, 2H, CH of C_6H_5O, *J* = 6.3 Hz), 5.54 (dd, 2H, CH of C_6H_5O, *J* = 1.5, 5.4 Hz), 6.11 (t, 1H, CH of C_6H_5O, *J* = 6.3 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 19.66, 28.97, 29.06, 55.04 (2C), 79.25 (2C), 81.49, 81.70 (2C), 93.56 (2C), 103.53, 156.78. HRMS(FAB-*m*-NBA): *m/z* calcd for $C_{14}H_{15}ORu$ 301.0170 (M^+ + H − 2H), found 301.0178 (M^+ + H − 2H). Anal. Calcd for $C_{14}H_{16}ORu$·0.5C_6H_5OH: C, 58.61; H, 5.50. Found: C, 59.11; H, 5.42.

Synthesis of Ru(η^5-C_6H_5O)(η^5-C_8H_9)·2C_6H_5OH (3·2C_6H_5OH). A mixture of Ru(η^6-cot)(dmfm)$_2$ (**1**) (250 mg, 0.50 mmol) and phenol (3.0 g) was placed in a two-necked 50 mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser under a flow of argon. The mixture was heated at 130 °C for 3 h with stirring. Then, the reaction mixture was cooled, and removal of excess phenol under vacuum at 100 °C led to a pale yellow solid of complex **3**·2C_6H_5OH, which was washed with pentane and diethyl ether (ca. 5 mL each) and vacuum-dried (150 mg, 61% yield). Crystals suitable for X-ray analysis were grown by layering pentane on a concentrated $CHCl_3$ solution at room temperature. Mp: 96.1−96.8 °C (dec). IR (KBr disk): 1604, 1590, 1522, 1464 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.25−2.40 (m, 6H, CH_2 of C_8H_9), 4.74 (t, 1H, CH of C_8H_9, *J* = 2.0 Hz), 4.79 (d, 2H, CH of C_8H_9, *J* = 2.0 Hz), 5.21 (t, 1H, CH of C_6H_5O, *J* = 5.4 Hz), 5.29 (d, 2H, CH of C_6H_5O, *J* = 6.8 Hz), 5.43 (dd, 2H, CH of C_6H_5O, *J* = 1.5, 5.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.36 (2C), 29.05, 70.00 (2C), 76.59 (2C), 76.59, 78.15 (2C), 84.52, 106.61, 150.16. HR-MS(FAB-*m*-NBA): *m/z* calcd for $C_{14}H_{15}ORu$ 301.0170 (M^+ + H), found 301.0165 (M^+ + H). Anal. Calcd for $C_{14}H_{14}ORu$·1.5C_6H_5OH: C, 62.71; H, 5.26. Found: C, 63.06; H, 5.29.

Synthesis of [Ru(η^6-C_6H_5OMe)(η^5-C_8H_9)]$^+$OTs$^-$ (4). A mixture of Ru(η^5-C_6H_5O)(η^5-C_8H_9)·2C_6H_5OH (**3**·2PhOH) (61.9 mg, 0.13 mmol), methyl *p*-toluenesulfonate (0.20 mL, 1.33 mmol), and THF (2.5 mL) was placed in a two-necked 20 mL Schlenk flask equipped with a magnetic stirring bar under a flow of argon. The mixture was stirred at room temperature for 12 h. The resulting solution was then concentrated to give the white residue of complex **4**, which was washed with pentane and diethyl ether (ca. 5 mL each) and vacuum-dried (46.4 mg, 74% yield). Crystals suitable for X-ray analysis were grown by layering pentane on a concentrated $CHCl_3$ solution at room temperature. Mp: 142.1−144.5 °C (dec). IR (KBr disk): 1700, 1683, 1664 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.35 (s, 3H, Me of OTs$^-$), 2.37−2.44 (m, 6H, CH_2 of pentalenyl), 3.81 (s, 3H, OMe), 5.22 (dd, 1H, CH of pentalenyl, *J* = 1.0,2.0 Hz), 5.23 (d, 2H, CH of pentalenyl, *J* = 2.0 Hz), 5.86 (t, 1H, CH of PhOMe, *J* = 5.9 Hz), 6.09 (t, 2H, CH of PhOMe, *J* = 5.9 Hz), 6.21 (d, 2H, CH of PhOMe, *J* = 6.8 Hz), 7.16 (d, 2H, CH of OTs$^-$, *J* = 8.8 Hz), 7.70 (d, 2H, CH of OTs$^-$, *J* = 7.8 Hz). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 21.38, 25.62 (2C), 29,42 (2C), 57.76, 73.67 (2C), 75.51 (2C), 82.45, 83.73, 85.30 (2C), 110.33, 125.15 (2C), 128.72, 134.43, 139.31. HR-MS(FAB-*m*-NBA): *m/z* calcd for $C_{15}H_{17}ORu$ 315.0327, found 315.0338 (M^+).

Dehydrogenative Ring-Closing Reaction of 2 to 3. A mixture of Ru(η^5-C_6H_5O)(η^5-C_8H_{11})·C_6H_5OH (**2**·PhOH) (138 mg, 0.35 mmol), phenol (1.0 g), and dimethyl fumarate (72.2 mg, 0.50 mmol) was placed in a two-necked 20 mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser under a flow of argon. The mixture was heated at 130 °C for 3 h with stirring. Then, the reaction mixture was cooled, and removal of excess phenol under vacuum at 100 °C led to a pale yellow solid, which was washed with pentane and diethyl ether (ca. 5 mL each) and vacuum-dried (**3**·2PhOH, 84% yield by NMR).

Crystallographic Study of Complexes 2, 3, and 4. The crystal data and experimental details for **2**, **3**, and **4** are summarized in Table 1. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The structures were solved by direct methods using SIR92[15] and expanded using Fourier techniques, DIRDIF99.[16] Hydrogen atoms were refined using the riding model. Neutral atom-scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_{calc};[18] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[19] The values for the mass attenuation coefficients were those

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of Creagh and Hubbell.[20] All calculations were performed using the CrystalStructure[21,22] crystallographic software package.

Theoretical Calculations. To consistently compare the single-point energies of model complexes, calculations were carried out using density functional theory (DFT) optimized geometries. Calculations were performed using the Gaussian 03 RevB.04[23] implementation of B3LYP [Becke three-parameter exchange functional (B3)[24] and the Lee−Yang−Parr correlation functional (LYP)[25]] on Intel PIV computers at the Kyoto University. The basis set is the combination of the Stuttgart−Dresden−Bonn energy-consistent pseudopotential (SDD)[26] for Ru and the 6-31G(d,p) basis set for all other hydrogen, carbon, and oxygen atoms. No constraints were imposed for all the systems. Frequency calculations on optimized species established that all the transition states possessed only one imaginary frequency. Zero-point energy and thermodynamic functions were computed at standard temperature (298.15 K) and pressure (1 atm). Spatial plots of the optimized geometries and frontier orbitals were obtained from Gaussian 03 output using Cambridge Soft Corporation's Chem 3D Pro v4.0 and Fujitsu WinMOPAC v3.5.

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Supporting Information Available: X-ray diffraction data for complexes **2**, **3**, and **4** in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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