1,8-Diphenylocta-1,3,5,7-tetraene Complexes of Ruthenium(II): Crystal Structures of [μ-(*s-cis*-1,2,3,4-η:*s-cis*-5,6,7,8-η-PhCH=CHCH=CHCH=CH-CH=CHPh)(RuClCp*)$_2$] and [μ-(*s-trans*-1,2,3,4-η:*s-trans*-5,6,7,8-η-PhCH=CHCH=CH-CH=CHCH=CHPh){Ru(acac)$_2$}$_2$]

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Reaction of 1,8-diphenyl-1,3,5,7-octatetraene with [Ru(μ-Cl)Cp*]$_4$ (**1**) (Cp* = η^5-pentamethylcyclopentadienyl) gave [μ-(*s-cis*-1,2,3,4-η:*s-cis*-5,6,7,8-η-PhCH=CHCH=CHCH=CH-CH=CHPh)(RuClCp*)$_2$] (**2**), whose crystal structure revealed that **2** has a planar tetraene backbone coordinated by two Cp*RuCl moieties in *s-cis*-η^4-fashion; while the reaction with Ru(acac)$_3$/Zn system resulted in the formation of [μ-(*s-trans*-1,2,3,4-η:*s-trans*-5,6,7,8-η-PhCH=CHCH=CHCH=CHCH=CHPh){Ru(acac)$_2$}$_2$] (**3**), where both of the two Ru(acac)$_2$ moieties prefer *s-trans* coordination and thus the plane of the octatetraene backbone of **3** is deformed into an S-shape. Electrochemical studies for complexes **2** and **3** revealed that they have a coupling between the two ruthenium centers and are conjugatively interacted dπ−pπ organometallic systems.

Introduction

π-Conjugated organic polymers have attracted much interest in view of their unique physical properties (conducting, photochemical, and nonlinear optical materials, etc.);[1,2] however, less attention has been given to π-conjugated polymers that incorporate transition metal complex chromophores into the organic polymer backbone.[3−8] Polyene is one of the most interesting π-conjugated compounds that bridge two metal centers.[9−14] On the other hand, the full complexation of polyenes with transition metals has rarely been reported so far.[15] This is expected to provide a unique pπ−dπ conjugated organometallic system; three categories (η^2-complexation[16] and two different η^4-complexations in *s-cis*- or *s-trans*-fashion[17]) being depicted in Scheme 1. These distinctive structural features of the diene complexes included in the polyene ligand prompted

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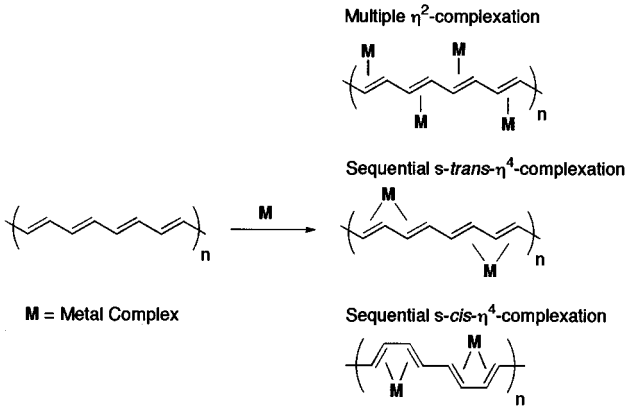
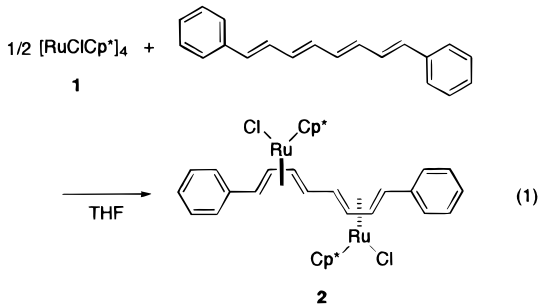
Scheme 1. Different Modes of Metal Coordination



us to synthesize tetraene complexes of ruthenium. We anticipated that this would be a model system leading to the formation of the fully metal-complexed poly(acetylene) system. Herein we report synthesis and characterization of the 1,8-diphenyl-1,3,5,7-octatetraene complexes bearing two different kinds of ruthenium fragments, RuCp*Cl (Cp* = η^5-pentamethylcyclopentadienyl) and Ru(acac)$_2$ (acac = acetylacetonate); these auxiliary ligands on the ruthenium atom controlling coordination modes (*s-cis* and *s-trans*) as well as conjugative interactions between metal centers.

Results and Discussion

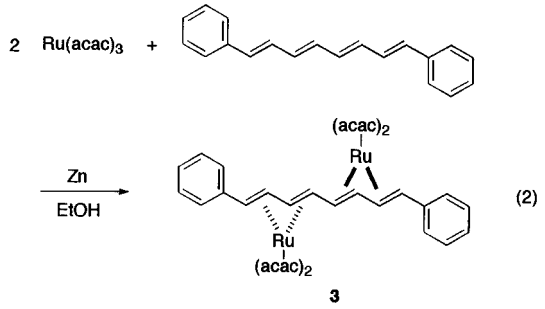
Reaction of [RuClCp*]$_4$ (**1**) with cyclic or acyclic diene is known to give ruthenium−diene complexes of the type of Cp*RuCl(diene).[18] Thus the reaction of **1** with (*E*,*E*,*E*,*E*)-1,8-diphenyl-1,3,5,7-octatetraene was investigated, hoping that this reaction would produce a dinuclear ruthenium(II) complex [μ-(*s-cis*-1,2,3,4-η:*s-cis*-5,6,7,8-η-PhCH=CHCH=CHCH=CHCH=CHPh)(RuClCp*)$_2$] (**2**). Addition of **1** to 2 equiv of (*E*,*E*,*E*,*E*)-1,8-diphenyl-1,3,5,7-octatetraene in THF led to the precipitation of **2** as red solids in 74% yield (eq 1). The



dinuclear structure of **2** was determined by analytical and spectroscopic data as well as X-ray crystallography; an ORTEP is shown in Figure 1 along with representative bond distances and angles. In the complex **2**, both of the two RuClCp* fragments coordinate to the two diene parts of the tetraene ligand in *s-cis* fashion. The dihedral angle (179.2(7)°) of C(1)−C(2)−C(3)−C(4) shows the planarity of the two diene units; which are related by the centrosymmetry, and thus all eight carbons of the tetraene ligand lie in a plane, indicating the longer π-conjugation of the tetraene backbone. In the absence of metal coordination, this type of (*s-cis*)-*trans*-polyene structure has not been found presumably due to the unfavorable steric congestion at the inner hydrogens. Bending back of these hydrogens on the Ru complexation is primarily responsible for the observed extensive planarity involving the two terminal phenyl groups.

When the reaction of **1** with an excess of the octatetraene in THF was carried out, the complexation of both diene units of the tetraene proceeded simultaneously and no predictable mononuclear complex was observed in contrast to the previously reported mononuclear Fe(CO)$_3$(η^4-1,8-diphenyl-1,3,5,7-octatetraene) complex, which involved a mixture of monometallic products.[17] Introduction of the RuClCp* moiety to one of the two diene parts of the tetraene would lower the LUMO level of the remaining diene part and thereby makes the adjacent diene moiety more reactive toward the latter introduction of the RuClCp* fragment.

Treatment of Ru(acac)$_3$ (acac = acetylacetonate) in the presence of zinc dust[19,20] with the octatetraene gave rise to another type of a dinuclear ruthenium tetraene complex, [μ-(*s-trans*-1,2,3,4-η:*s-trans*-5,6,7,8-η-PhCH=CHCH=CHCH=CHCH=CHPh){Ru(acac)$_2$}$_2$] (**3**) in 74% yield (eq 2). In good agreement to the case of **2**, an



analogous reaction with an excess of the tetraene ligand resulted in the exclusive formation of **3**. The centrosymmetric dinuclear structure of **3** has been determined crystallographically (Figure 2). Most significant feature is that both of the two octahedral Ru(acac)$_2$ fragments prefer *s-trans* coordination and *anti*-position each other. Thus the plane of the octatetraene backbone of **3** is deformed, in contrast to **2**, into an S-shape; therefore the torsion angle of C(1)−C(2)−C(3)−C(4) being 128(1)°. This deformation of the diene unit has already been observed in mononuclear *s-trans* diene complexes such as ZrCp$_2$(*s-trans*-η^4-PhCH=CHCH=CHPh),[21] NbCp(*s-cis*-η^4:*s-trans*-η^4-2,4,7,9-$C_{14}H_{22}$),[22] MoCp(NO)(*s-trans*-η^4-2,4-C_8H_{14}),[23] and Ru(acac)$_2$(η^4-1,3-diene).[19,20] The bond distances of Ru−O lie in the range of 2.027(9)−2.051(10) Å as expected for *s-trans*-diene complexes of Ru(acac)$_2$(diene).[19,20]

The cyclic voltammograms of the dinuclear tetraene complexes **2** and **3** were measured together with those

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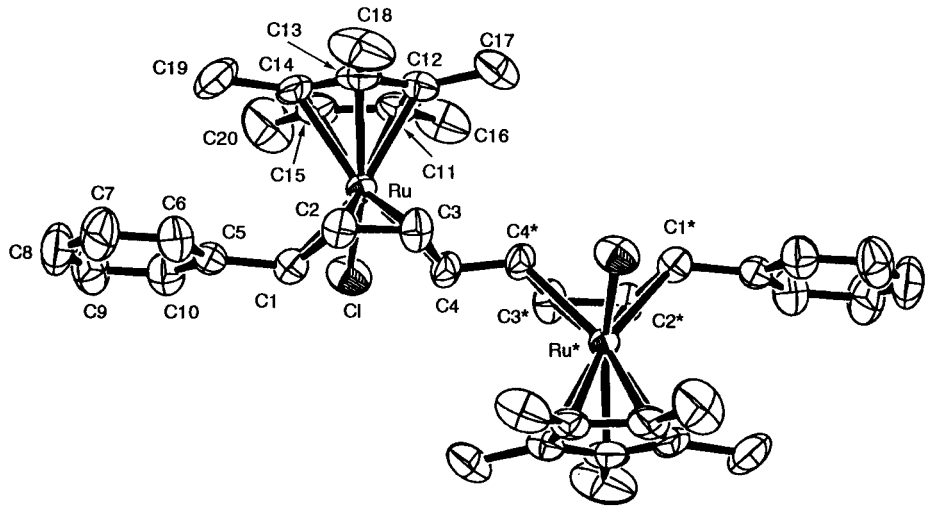

Figure 1. *ORTEP* drawing of complex **2** with the atom numbering scheme. Selected bond lengths (Å), angles (deg), and torsion angles (deg): Ru−Cl = 2.445(1), Ru−C(1) = 2.270(4), Ru−C(2) = 2.167(4), Ru−C(3) = 2.163(4), Ru−C(4) = 2.275(4), C(1)−C(2) = 1.399(5), C(2)−C(3) = 1.436(5), C(3)−C(4) = 1.381(6), C(4)−C(4)* = 1.453(7); Cl−Ru−C(1) = 84.7(1), Cl−Ru−C(4) = 82.0(1), C(1)−Ru−C(4) = 78.7(1), Ru−C(1)−C(2) = 67.6(2), Ru−C(4)−C(3) = 67.5(2), C(1)−C(2)−C(3) = 121.1(4), C(2)−C(3)−C(4) = 121.5(4); C(1)−C(2)−C(3)−C(4) = 179.2(7), C(3)−C(4)−C(4)*−C(3)* = 180.

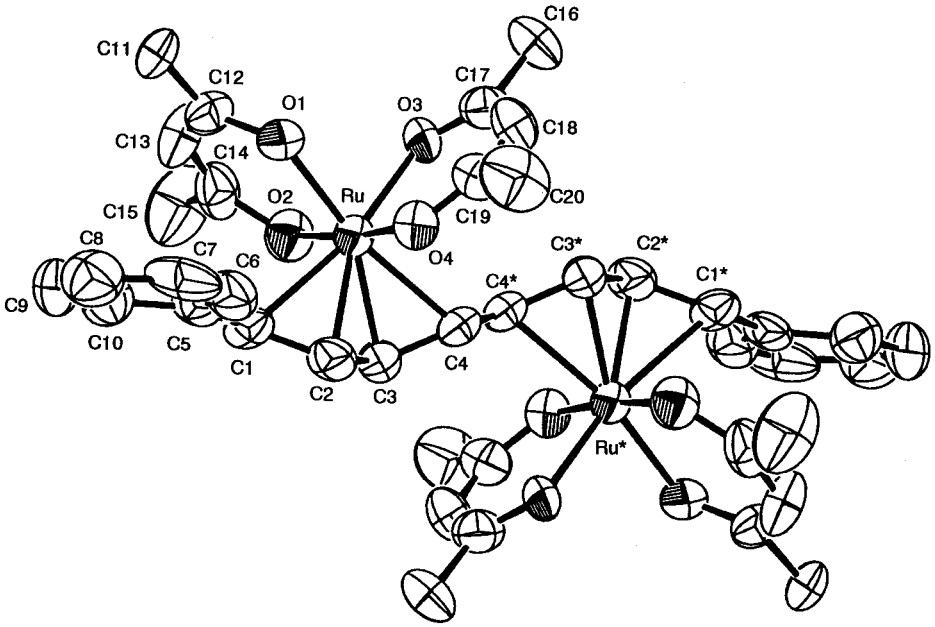

Figure 2. *ORTEP* drawing of complex **3** with the atom numbering scheme. Selected bond lengths (Å), angles (deg), and torsion angles (deg): Ru−O(1) = 2.040(8), Ru−O(2) = 2.027(9), Ru−O(3) = 2.043(8), Ru−O(4) = 2.051(10), Ru−C(1) = 2.29(1), Ru−C(2) = 2.10(1), Ru−C(3) = 2.11(1), Ru−C(4) = 2.27(1), C(1)−C(2) = 1.38(2), C(2)−C(3) = 1.44(2), C(3)−C(4) = 1.37(2), C(4)−C(4)* = 1.45(2); O(1)−Ru−O(2) = 92.9(4), O(1)−Ru−O(3) = 84.2(4), O(1)−Ru−O(4) = 82.8(4), O(2)−Ru−O(3) = 84.3(4), O(2)−Ru−O(4) = 175.0(4), O(3)−Ru−O(4) = 92.6(4), C(1)−Ru−C(4) = 100.7(5), C(1)−C(2)−C(3) = 119(1), C(2)−C(3)−C(4) = 119(1); C(1)−C(2)−C(3)−C(4) = 128(1), C(2)−C(3)−C(4)−C(4)* = −167(1), C(3)−C(4)−C(4)*−C(3)* = 180.

of mononuclear 1,4-diphenyl-1,3-butadiene complexes, Cp*RuCl(*s-cis*-η^4-PhCH═CHCH═CHPh) (**4**) and Ru(acac)$_2$(*s-trans*-η^4-PhCH═CHCH═CHPh) (**5**) in different solvents. A reversible or quasireversible oxidation was observed at $E_{1/2}$ = + 0.33 V for complex **4** and $E_{1/2}$ = + 0.40 V vs Fc^+/Fc for **5**. On the other hand, dinuclear complexes **2** and **3** showed a strong solvent dependence on the cyclic voltammogram. The cyclic voltammogram of **2** in 1,2-dichloroethane showed an irreversible two-electron oxidation wave with an E_p value of + 0.16 V at 100 mV/s. However, at faster scan rate (>10 V/s) another quasi-reversible wave at +0.25 V was observed in addition to the reversible first wave at +0.09 V, indicating the successive one-electron processes followed by fast chemical reactions. This observation allows us to evaluate approximate potential separation between the first and the second processes. On the other hand, complex **3** showed two quasireversible one-electron oxidation waves at $E_{1/2}$ = +0.29 and +0.46 V at −50 °C. Since the differences in potential between the half-reactions of the successive electron transfers can depend upon the extent of interaction between the sites, the potential separation for complex **3** ($\Delta E_{1/2}$ = 170 mV) is comparable to that for complex **2** ($\Delta E_{1/2}$ = ca. 160 mV), indicating a coupling between the metal centers (conjugated dπ−pπ organometallic systems). When the CV

measurement was performed in polar solvent such as acetone or THF, the cyclic voltammograms of **2** and **3** showed only irreversible oxidation wave(s) ($E_p = +0.06$ V for complex **2**; +0.31 and +0.50 V for **3** in acetone, and $E_p = +0.15$ V for **2**; +0.35 V vs Fc^+/Fc for **3** in THF, both at 100 mv/s, respectively), indicating that solvent plays an important role for the oxidation processes of these complexes.

In summary, we have demonstrated that it is possible to control the coordination mode of the diene units in the tetraene ligand by varying the auxiliary ligand on the ruthenium metal. We found that the complexation of the tetraene with two ruthenium moieties occurred concurrently, and thus the complete complexation of much longer π-conjugated polyene system with the ruthenium fragments would be expected instead of partial ones. We are presently engaged in attempts to prepare fully coordinated multinuclear ruthenium complexes of polyenes as well as poly(alkyne)s, both of which are expected to be new dπ−pπ bonded electronic materials.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by using the standard Schlenk techniques under an argon atmosphere. THF, hexane, toluene, and ether were dried over sodium benzophenone ketyl. Dichloromethane was purified by distillation after drying over CaH_2. Ethanol was distilled from magnesium ethoxide. 1,4-Diphenyl-1,3-butadiene and 1,8-diphenyl-1,3,5,7-octatetraene were purchased from Aldrich Chemical Co., Inc. Complexes $[Ru(\mu_3\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_4$ (**1**) and $Ru(acac)_3$ were prepared according to the literature procedure.[1,2]

Nuclear magnetic resonance [^{1}H(400 and 270 MHz) and ^{13}C (400 MHz) NMR] spectra were measured on a JEOL JNM-GSK400 or a JEOL JNM-EX270 spectrometer. Other spectra were recorded by the use of the following instruments: IR, Hitachi 295; low- and high-resolution mass spectra, JEOL SX-102; UV/vis spectra, Jasco Ubest-30 and Shimadzu UV-265FS. X-ray crystallographic studies were performed on a Rigaku AFC-7 diffractometer interfaced with the TEXSAN computer system. Elemental analyses were performed at Elemental Analysis Center, Faculty of Science, Osaka University. All melting points were measured in sealed tubes and were not corrected.

Electrochemical measurements were made at room temperature as well as −50 °C with a BAS 100 B/W electrochemical workstation. The working electrode was a platinum disk electrode and the auxiliary electrode was a platinum wire. The reference electrode was $Ag/AgNO_3$ (0.01 M in 0.1 M $TBABF_4$-CH_3CN), abbreviated as Ag/Ag^+. The $E_{1/2}$ value for the ferrocenium/ferrocene (Fc^+/Fc) couple is +0.23 V *vs* Ag/Ag^+. All potential values are reported *vs* Fc^+/Fc.

Preparation of 2. To a suspension of $[Ru(\mu_3\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_4$ (**1**) (1.084 g, 1.00 mmol) in THF (50 mL) was added 1,8-diphenyl-1,3,5,7-octatetraene (0.513 g, 1.99 mmol) at 25 °C. The color of the mixture turned to bright red, and then red solid was precipitated. After 3 h, the red precipitation was collected and then washed with hexane. Recrystallization from dichloromethane afforded **2** (1.18 g, 74% yield) as red microcrystals, mp 220−230 °C (dec). ^{1}H NMR ($CDCl_3$, 35 °C): δ 1.36 (s, 30H, C_5Me_5), 2.97 (dd, 2H, H_4, J = 6.5 and 2.6 Hz), 3.57 (d, 2H, H_1, J = 10.1 Hz), 5.10−5.30 (m, 4H, H_2 and H_3), 7.17−7.52 (m, 10H, C_6H_5). FAB MS (NBA matrix): *m*/*z* 802 (M^+). UV/vis (CH_2Cl_2): λ_{max} 518 nm ($\epsilon = 1.14 \times 10^4$ M^{-1} cm^{-1}). Anal. Calcd for $C_{40}H_{48}Cl_2Ru_2$: C, 59.90, H, 6.03. Found: C, 59.64, H, 5.74.

Table 1. Crystal and Refinement Data for 2 and 3

complex	**2**	**3**
formula	$C_{40}H_{48}Cl_2Ru_2$	$C_{41}H_{48}O_8Cl_2Ru_2$
fw	801.87	941.87
cryst system	monoclinic	monoclinic
space group	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a, Å	8.342(3)	12.140(3)
b, Å	18.412(2)	15.367(2)
c, Å	11.687(2)	13.122(3)
β, deg	92.69(2)	106.70(1)
Z	2	2
V, Å^3	1792.9(6)	2344.8(7)
d_{calcd}, g cm^{-3}	1.485	1.334
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
no. of reflcns measd	$+h, +k, \pm l$	$+h, +k, \pm l$
no. of crystal size, mm	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.3
abs coeff, cm^{-1}	10.18	6.85
scan mode	$\omega-2\theta$	$\omega-2\theta$
temp, °C	20	20
$2\theta_{max}$, deg	55.0	55.0
no. of data colcd	4535	5840
no. of unique data	4254 (R_{int} = 0.015)	5585 (R_{int} = 0.030)
no. of observns	3233 ($I > 1.50\sigma(I)$)	2522 ($I > 3.00\sigma(I)$)
no. of variables	199	243
R^a	0.036	0.074
$R_w{}^b$	0.028	0.065
GOF	2.39	4.13
Δ, e Å^{-3}	0.48 (max) −0.47 (min)	1.80 (max) −1.05 (min)

^{a} $R = \sum||F_o| - |F_c||/|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. $w = 1/\sigma^2(F_o)$; function minimized: $\sum w(|F_o| - |F_c|)^2$.

Preparation of 3. To $Ru(acac)_3$ (0.400 g, 1.00 mmol) in ethanol (30 mL) was added 1,8-diphenyl-1,3,5,7-octatetraene (0.129 g, 0.500 mmol) and zinc dust (activated by HCl, 0.13 g). The reaction mixture was refluxed for 12 h until the color turned to orange. The solvent was removed in vacuo, and then the residue was extracted with toluene (40 mL). The remained zinc dust and $Zn(acac)_2$ were removed by centrifugation. The supernatant was concentrated and then cooled at −20 °C, affording **3** (0.32 g, 74% yield) as yellow-orange solids, mp 165−170 °C (dec). ^{1}H NMR (CD_2Cl_2, 35 °C): δ 1.61 (s, 6H, acac methyl), 1.90 (s, 6H, acac methyl), 1.97 (s, 6H, acac methyl), 2.31 (s, 6H, acac methyl), 3.72 (m, 2H, H_3), 4.06 (m, 2H, H_4), 4.47 (m, 4H, H_1 and H_2), 5.40 (s, 2H, acac methine), 5.57 (s, 2H, acac methine), 7.13−7.23 (m, 10H, C_6H_5). FAB MS (NBA matrix): *m*/*z* 858 (M^+). IR (Nujol): ν (CO)/cm^{-1} 1560 (m), 1545 (w), 1520 (s). UV/vis (CH_2Cl_2): λ_{max} 340 nm ($\epsilon = 0.26 \times 10^4$ M^{-1} cm^{-1}). Anal. Calcd for $C_{40}H_{46}O_8Ru_2$: C, 56.05, H, 5.41. Found: C, 55.70, H, 5.54.

Preparation of 4. To a suspension of $[Ru(\mu_3\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_4$ (**1**) (0.544 g, 0.500 mmol) was added 1,4-diphenyl-1,3-butadiene (0.413 g, 2.00 mmol) at room temperature. The reaction mixture was stirred for 3 h. The color of the solution turned to bright red. After the solvent was removed under reduced pressure, the resulting residue was extracted with dichloromethane (40 mL). The extract was concentrated to ca 5 mL and cooled at −20 °C for 12 h, affording **4** as red crystals (0.75 g, 78% yield), mp 175−180 °C (dec). ^{1}H NMR ($CDCl_3$, 35 °C): δ 1.16 (s, 15H, C_5Me_5), 3.81 (dd, 2H, J = 14.6 and 4.7 Hz), 5.33 (dd, 2H), 7.18−7.57 (m, 10H, C_6H_5). FAB MS (NBA matrix): *m*/*z* 478 (M^+). UV/vis (CH_2Cl_2): λ_{max} 481 nm ($\epsilon = 0.59 \times 10^4$ $M^{-1}cm^{-1}$). Anal. Calcd for $C_{26}H_{29}ClRu$: C, 65.31, H, 6.11. Found: C, 65.18, H, 5.99.

Preparation of 5. To a suspension of $Ru(acac)_3$ (0.200 g, 0.502 mmol) in ethanol (30 mL) was added 1,4-diphenyl-1,3-butadiene (0.103 g, 0.499 mmol) and zinc dust (activated by HCl, 0.13 g). The reaction mixture was refluxed for 12 h until the color turned to orange. The solvent was removed in vacuo, and the residue was extracted with toluene (40 mL). After the extraction was concentrated to ca. 5 mL, crystallization from toluene at −20 °C afforded **5** (0.15 g, 58% yield) as orange microcrystals, mp 191−197 °C (dec). ^{1}H NMR (C_6D_6, 35 °C):

δ 1.56 (s, 6H, acac methyl), 1.77 (s, 6H, acac methyl), 4.52 (dd, 2H, J = 8.7 and 2.2 Hz), 4.70 (dd, 2H), 5.30 (s, 2H, acac methine), 7.01−7.42 (m, 10H, C_6H_5). FAB MS (NBA matrix): m/z 506 (M^+). IR (Nujol): ν (CO)/cm^{-1} 1568 (s), 1515 (s). UV/vis (CH_2Cl_2): λ_{max} 325 nm ($\epsilon = 0.13 \times 10^4$ M^{-1} cm^{-1}). Anal. Calcd for $C_{26}H_{28}O_4Ru$: C, 61.76, H, 5.58. Found: C, 61.49, H, 5.54.

Crystallographic Data Collection and Structure Determination of 2 and 3. Data Collection. Crystals of **2** and **3** (Table 1) suitable for X-ray diffraction studies were sealed in glass capillaries under argon atmosphere, and then each crystal of complexes was mounted on a Rigaku AFC-7R four-circle data collection using Mo Kα radiation. The unit cell parameters at 23 °C were determined by a least-squares fit to 2θ values of 25 strong higher reflections for all complexes. Three standard reflections were chosen and monitored every 150 reflections. Empirical absorption correction was carried out based on an azimuthal scan. Every sample showed no significant intensity decay during the data collection.

Structure Determination and Refinement. The structures of all complexes were solved by direct method (SHELXS 86)[24] and refined by the full-matrix least-squares method. In the subsequent refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$, where $w^{-1} = \sigma^2(F_o) = \sigma^2(F_o^2)/(4F_o^2)$. The positions of all non-hydrogen atoms for all complexes were found from a difference Fourier electron density map and refined anisotropically. All hydrogen atoms for each complex were placed in calculated positions (C−H = 0.95 Å) and kept fixed. All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

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Supporting Information Available: Final positional parameters, final thermal parameters, bond distances, angles, and torsion angles for the complexes **2** and **3** (30 pages). Ordering information is given on any current masthead page.

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