

Unique Preferential Conformation and Movement of Ru(acac)₂ Fragment(s) Coordinated in an η^4 -*s-trans* Fashion to All Diene Unit(s) of α,ω -Diphenylpolyenes

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α,ω -Diphenylpolyene complexes bearing bis(acetylacetonato)ruthenium(II) of the general formula Ru_n(acac)_{2n}(polyene) [**1**: $n = 1$, polyene = 1,4-diphenylbuta-1,3-diene; **2**: $n = 1$, polyene = 1,6-diphenylhexa-1,3,5-triene; **3**: $n = 2$, polyene = 1,8-diphenylocta-1,3,5,7-tetraene; **4** and **6**: $n = 2$, polyene = 1,10-diphenyldeca-1,3,5,7,9-pentaene; **5**: $n = 3$, polyene = 1,12-diphenyldodeca-1,3,5,7,9,11-hexaene] were prepared by reaction of Ru(acac)₃ with the corresponding polyene in the presence of excess amounts of zinc dust. The Ru(acac)₂ fragments in **1–6** coordinated in an η^4 -*s-trans* fashion to each diene unit of the polyene ligands. The Δ -Ru(acac)₂ unit and its enantiomer Λ -Ru(acac)₂ were assigned to coordinate to the *re*-face and the *si*-face of the diene unit, respectively, on the basis of the crystal structure of complexes **1** and **2** together with the previously reported **3**. Hexaene complex **5** was assumed to have the structure *anti,anti*- Δ,Λ -**5a**, and its enantiomer, *anti,anti*- Λ,Δ -**5b**. Pentaene complex **4**, in which two Ru(acac)₂ fragments were bound to C(1)–C(4) and C(7)–C(10) of the pentaene ligand, was isolated. The Ru(acac)₂ fragment of **4** moved over the pentaene in CHCl₃ to settle in the thermodynamically stable **6**, in which two ruthenium fragments are located at adjacent positions. The metal migration process, as monitored by the decrease of **4**, was found to be of first-order for **4**, giving the activation parameter $\Delta G^\ddagger(25^\circ\text{C}) = 15.8 \pm 0.2$ kcal/mol.

Introduction

One-dimensional π -conjugated polymers¹ and their metal complexes² are attractive materials for showing unique chemical, electrical, and optical properties originating from the delocalization of π -electrons along their polymer main chains. Polyacetylene is the most fundamental one-dimensional π -conjugated polymer, and active investigations have been carried out since the discovery of its conducting doped films.³ Polyacetylene might act as olefin or conjugated diene units that can coordinate to various transition metal compounds.⁴ Thus, incorporation of transition metal chromophores

led to $p\pi$ - $d\pi$ conjugated organometallic systems that have several features: hapticity (η^2 , η^4 , etc.), various coordination modes (*s-cis*⁵ or *s-trans*⁶ modes for diene complexation), stereochemistry (*syn* or *anti* for polynuclear complexes), nuclearity (mononuclear,^{5,6} dinuclear,⁷ polynuclear,⁸ etc.), and fluxionality.^{9,10} However, polyacetylene is sensitive to air and insoluble in any organic solvent, resulting in the difficulty of handling its metal complexes. As a partial model system, we focused on the use of α,ω -diphenylpolyenes, Ph-

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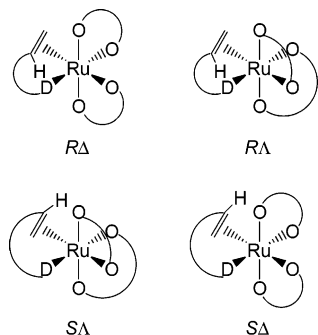


Figure 1. Four isomers of alkene complexes of Ru(acac)₂ (alkene with a donor ligand).

(CH=CH)_nPh,¹¹ which are stable in air and act as unique, versatile ancillary ligands for transition metals. We have already prepared two dinuclear tetraene complexes bearing RuClCp* (Cp* = C₅Me₅) or Ru(acac)₂ and have found that the tetraene ligand was flexible, which enabled its coordination to RuClCp* in an *s-cis*- η^4 fashion and to Ru(acac)₂ in an *s-trans*- η^4 fashion.^{12a} Kurosawa et al. recently reported several linear palladium cluster complexes supported by two polyene ligands.^{7e,f,8,12b}

In this paper, we report that the Ru(acac)₂ fragment coordinated in an *s-trans* fashion to α,ω -diphenylpolyene (polyene = diene, triene, tetraene, pentaene, and hexaene) to give mononuclear, dinuclear, and trinuclear ruthenium-polyene complexes. We found that all diene units are fully metalated, and one double bond remained intact in triene and pentaene complexes. Since Bennett et al. demonstrated that alkenes with a donor moiety coordinated to Ru(acac)₂ to form four diastereomers ($R\Delta$, $S\Delta$; $R\Lambda$, $S\Lambda$) (Figure 1),¹³ the diastereochemistry of the polyene complexes of Ru(acac)₂ has been described. Structural characterization of these complexes, as well as the unique movement of the ruthenium fragment in the pentaene complex, is the subject of this paper.

Results

Preparation and Characterization of Bis(acetylacetonato)ruthenium(II) Complexes of α,ω -Diphenyl-

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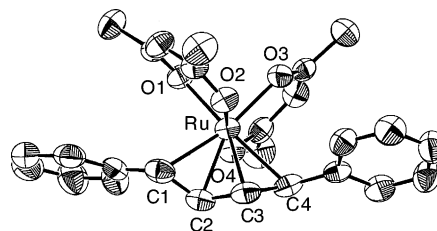
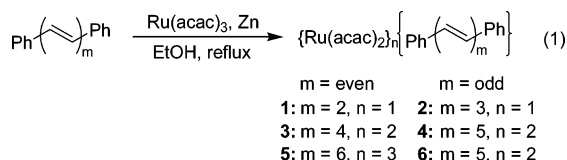


Figure 2. ORTEP drawing of complex **1** with the atom-numbering scheme. The enantiomer, Δ -**1a**, is shown.

ylpolyenes. The treatment of α,ω -diphenylpolyenes with Ru(acac)₃ in the presence of excess amounts of zinc dust in ethanol afforded the corresponding bis(acetylacetonato)ruthenium(II) complexes of the general formula Ru_n(acac)_{2n}(polyene) [**1**: *n* = 1, polyene = 1,4-diphenylbuta-1,3-diene; **2**: *n* = 1, polyene = 1,6-diphenylhexa-1,3,5-triene; **3**: *n* = 2, polyene = 1,8-diphenylocta-1,3,5,7-tetraene; **4** and **6**: *n* = 2, polyene = 1,10-diphenyldeca-1,3,5,7,9-pentaene; **5**: *n* = 3, polyene = 1,12-diphenyldodeca-1,3,5,7,9,11-hexaene] (eq 1), where odd-numbered polyene complexes **2** and **4** (and its isomer **6**) have a free olefinic part. Each Ru(acac)₂ fragment coordinated in an η^4 -*s-trans* fashion to each diene unit of the polyene. All complexes show IR bands in the region 1600–1500 cm⁻¹ due to the C=O group of the acac ligand bound to the ruthenium atom.^{6f,g} The twisted η^4 -*s-trans*-diene ruthenium configuration was confirmed by ¹H NMR spectroscopy: the coupling constants of the outer protons and the inner protons of the diene unit bound to the ruthenium center lie in the range ³*J* = 10–11 Hz, while the coupling constant between the inner protons of the diene moiety was found to be 7–8 Hz, which is comparable to the coupling constants (³*J* = 7–8 Hz) between the inner protons observed for the typical *s-trans*-diene bound to mononuclear transition metals.^{6h,i,14}



The single-crystal X-ray analysis of **1** (Figure 2 and Table 1), together with its ¹H NMR spectrum, revealed that Δ -**1a** and its Λ -enantiomer, Λ -**1b**,¹⁵ were predominantly formed. This indicates that Δ -Ru(acac)₂ and Λ -Ru(acac)₂ fragments thermodynamically favored the *re*- and *si*-faces of 1,4-diphenylbuta-1,3-diene, respectively. The NMR spectral data and results of X-ray analysis of **3** indicated that the structure of dinuclear tetraene complex **3** is *anti*- Δ , Λ -**3a**,^{12a} which is consistent with the preferential geometry of **1**. The steric hindrance between two Ru(acac)₂ fragments ruled out *syn*-isomers.^{12a}

Trinuclear hexaene complex **5** was isolated in 10% yield. The ¹H NMR spectrum of **5** in CDCl₃ showed only one set of six olefinic protons together with three

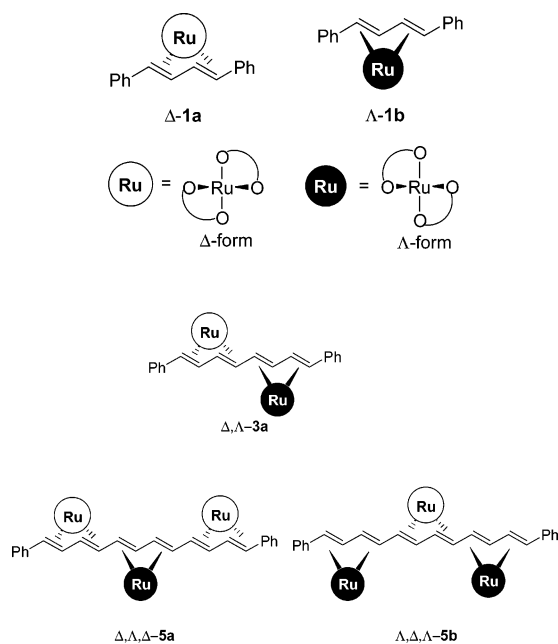
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(15) For distinguishing isomers, we named all isomers by using the number with "a" and "b", which stand for a ruthenium fragment bound to a C1–C4 diene unit from the *re*-face and *si*-face, respectively.

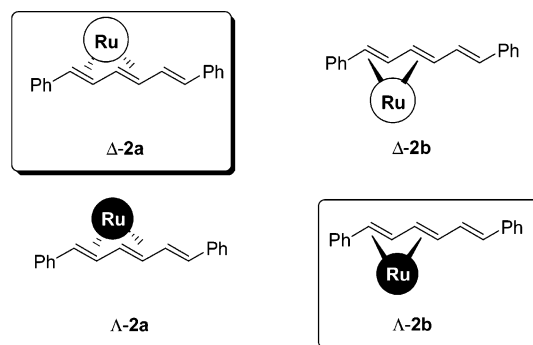
Table 1. Selected Bond Distances and Angles of 1

Distances (Å)			
Ru–O(1)	2.048(2)	Ru–O(2)	2.052(2)
Ru–O(3)	2.045(2)	Ru–O(4)	2.059(2)
Ru–C(1)	2.259(3)	Ru–C(2)	2.114(3)
Ru–C(3)	2.110(3)	Ru–C(4)	2.285(3)
C(1)–C(2)	1.380(4)	C(2)–C(3)	1.447(4)
C(3)–C(4)	1.391(4)		
Angles (deg)			
O(1)–Ru–O(2)	92.44(8)	O(1)–Ru–O(3)	84.87(8)
O(1)–Ru–O(4)	83.55(8)	O(2)–Ru–O(3)	82.26(8)
O(2)–Ru–O(4)	173.89(8)	O(3)–Ru–O(4)	92.77(8)
C(1)–Ru–C(2)	36.6(1)	C(1)–Ru–C(3)	67.8(1)
C(1)–Ru–C(4)	101.3(1)	C(2)–Ru–C(3)	40.1(1)
C(2)–Ru–C(4)	66.5(1)	C(3)–Ru–C(4)	36.6(1)
Ru–C(1)–C(2)	66.0(2)	Ru–C(2)–C(3)	69.8(2)
Ru–C(3)–C(4)	78.5(2)	Ru–C(2)–C(1)	77.4(2)
Ru–C(3)–C(2)	70.1(2)	Ru–C(4)–C(3)	64.9(2)
C(1)–C(2)–C(3)	119.4(3)	C(2)–C(3)–C(4)	116.7(3)
Torsion Angles (deg)			
C(1)–C(2)–C(3)–C(4)	126.9(3)		

methine signals due to the acetylacetonato groups being in a 1:1:1 integration ratio. These data indicated that **5** has a C_2 -axis passing through the central ruthenium atom and the center of the polyene ligand. On the basis of the preferential geometries of **1** and **3**, where the Δ -Ru(acac)₂ and the Λ -Ru(acac)₂ units preferentially coordinate to *re*- and *si*-faces of the polyene ligand, respectively (vide supra), it is assumed that complex **5** has the structure *anti,anti*- Δ,Δ,Δ -**5a**, and its enantiomer, *anti,anti*- Λ,Λ,Λ -**5b**. No partially metalated complex with one or two Ru(acac)₂ fragments was obtained, indicating that sequential complexation with ruthenium spontaneously proceeded to give only the fully metalated complex **5**. The coordination of a ruthenium fragment to a diene unit lowered the HOMO level of the adjacent diene unit of the polyene so that the following ruthenium fragment can readily coordinate to it. Additionally, the coupling constant (10.3 Hz) of the terminal protons (H4, H5, and H8, H9) between two *s-trans*-diene units suggested an all-*trans* geometry of the whole hexaene moiety.



In contrast to polyene complexes **1**, **3**, and **5**, which contain even numbers of olefinic units, complexes **2** and

Scheme 1

4 (and its isomer **6**), with odd numbers of olefinic units, have an uncoordinated C=C moiety on their polyene backbone, as evident from their ¹H NMR spectra. The conformational preference for these complexes was not controlled since we obtained these complexes as a mixture of isomers. The ¹H NMR spectrum of **2** in CDCl₃ indicated that there are two sets of signals due to two magnetically nonequivalent isomers, Δ -**2a** and Δ -**2b** (and their enantiomers, Λ -**2a** and Λ -**2b**) in a 2:1 integral ratio (Scheme 1). There was no equilibrium between the two isomers, as judged from the results of variable-temperature ¹H NMR spectroscopy. Each isomer shows signals between 5 and 7 ppm, which are assignable to the protons of a free C=C part. The major isomer is determined to be Δ -**2a** and Λ -**2b** from the crystal structure of complex **2**, which is consistent with the preferred coordination mode of the Ru(acac)₂ unit, as found for **1** and **3**.

Figure 3 shows the molecular structure of Λ -**2b**. Δ -**2a** is also included in the crystal because of the centrosymmetric space group $P2_1/a$. Complex **2** has a structural feature similar to that found for diene complex **1**; the Δ -Ru(acac)₂ fragment favors the *re*-face of the triene ligand. As shown in Table 2, the bond distances of C(1)–C(2), C(2)–C(3), and C(3)–C(4) are 1.370(5), 1.436(6), and 1.360(6) Å, respectively. The observed short–long–short pattern of the carbon–carbon bonds is typical for an *s-trans*-1,3-diene ligand bound to a ruthenium atom.^{6f,g,i} The bond distance (1.309(6) Å) of C(5)–C(6) is normal for a free C=C bond. Not only the diene unit coordinating to the ruthenium atom but also the remaining olefin part of the triene ligand adopts the *s-trans* geometry, although the torsion angle (128.1(5)°) of C(1)–C(2)–C(3)–C(4) indicates that the diene unit is greatly deformed compared with that of C(4)–C(5)–C(6)–C(13) (178.7(4)°). The bond distances of Ru–O lie in the range 2.050(3)–2.063(3) Å, which is in good accordance with those reported for Ru(acac)₂(diene) complexes.^{6f,g,i}

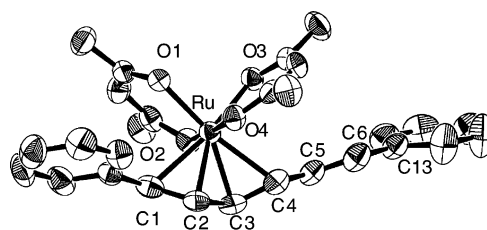
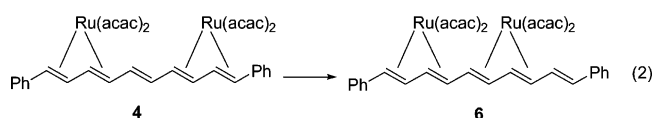


Figure 3. ORTEP drawing of triene complex **2** with the atom-numbering scheme. The enantiomer, Λ -**2b**, is shown.

Table 2. Selected Bond Distances and Angles of **2**

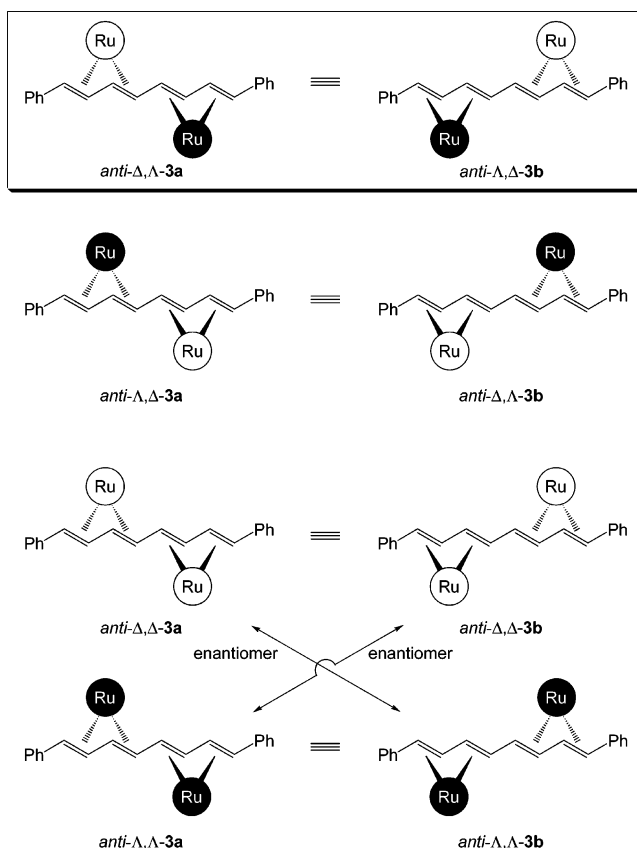
Distances (Å)			
Ru–O(1)	2.050(3)	Ru–O(2)	2.054(3)
Ru–O(3)	2.056(3)	Ru–O(4)	2.063(3)
Ru–C(1)	2.281(4)	Ru–C(2)	2.100(4)
Ru–C(3)	2.099(4)	Ru–C(4)	2.275(4)
C(1)–C(2)	1.370(5)	C(2)–C(3)	1.436(6)
C(3)–C(4)	1.360(6)	C(4)–C(5)	1.448(6)
C(5)–C(6)	1.309(6)		
Angles (deg)			
O(1)–Ru–O(2)	92.8(1)	O(1)–Ru–O(3)	86.0(1)
O(1)–Ru–O(4)	85.1(1)	O(2)–Ru–O(3)	83.3(1)
O(2)–Ru–O(4)	174.4(1)	O(3)–Ru–O(4)	91.4(1)
C(1)–Ru–C(2)	36.1(1)	C(1)–Ru–C(3)	66.8(2)
C(1)–Ru–C(4)	100.7(2)	C(2)–Ru–C(3)	40.0(2)
C(2)–Ru–C(4)	67.2(2)	C(3)–Ru–C(4)	36.0(1)
Ru–C(1)–C(2)	64.7(3)	Ru–C(2)–C(3)	70.0(2)
Ru–C(3)–C(4)	79.1(3)	Ru–C(2)–C(1)	79.1(3)
Ru–C(3)–C(2)	70.1(2)	Ru–C(4)–C(3)	65.0(3)
C(1)–C(2)–C(3)	118.9(5)	C(2)–C(3)–C(4)	120.2(4)
C(3)–C(4)–C(5)	126.9(5)	C(4)–C(5)–C(6)	124.7(5)
Torsion Angles (deg)			
C(1)–C(2)–C(3)–C(4)	128.1(5)	C(4)–C(5)–C(6)–C(13)	178.7(4)

The pentaene complex was isolated in 81% yield. NMR and mass spectral data, together with results of combustion analysis, confirmed that the pentaene complex has two Ru(acac)₂ fragments, and accordingly, one C=C bond remained intact. There are two possible isomers, **4** and **6**, if the chirality of the Ru(acac)₂ fragments is neglected (eq 2). The isolated compound was assigned as **4**, which was found to be stable in benzene solution. The ¹H NMR spectrum of **4** in C₆D₆ displayed one set of five proton signals due to the pentaene ligand, indicating that the two ruthenium fragments were coordinated in an η^4 -*s-trans* fashion at C1–C4 and C7–C10, the central double bond (C5–C6) remained intact, and the pentaene ligand has the all-*transoid* conformation.



When complex **4** was dissolved in CDCl₃, the ¹H NMR spectrum gradually changed and displayed 10 new magnetically nonequivalent protons of the pentaene ligand due to another isomer, **6**. NMR spectroscopy revealed the final ratio of **4** and **6** to be 1:4. The two signals observed at δ 6.26 and 6.58 were assignable to H⁹ and H¹⁰, suggesting that the C(9)–C(10) double bond of **6** is uncoordinated. The other eight signals of the pentaene ligand of **6** lie in the region δ 3.67–4.47 and are assignable to the protons of the two neighboring diene units bound in an η^4 -*s-trans* fashion to two ruthenium atoms. The ¹H NMR spectrum also exhibited a total of eight nonequivalent signals (δ 1.55–2.32) due to the methyl protons of four acac ligands for two nonequivalent Ru(acac)₂ fragments.

As shown by eq 2, one of the two Ru(acac)₂ fragments of **4** moved along the pentaene ligand to give **6** in chloroform solution. This is the second example of organometallic fragment movement over a linear polyene system: Fe(CO)₅(1-phenyl-6-(*p*-tolyl)-1,3,5-hexatriene) was previously reported by Whitlock et al.¹⁰ Thermodynamic parameters of this process were monitored by ¹H NMR spectroscopy in the temperature range 15–27

Scheme 2

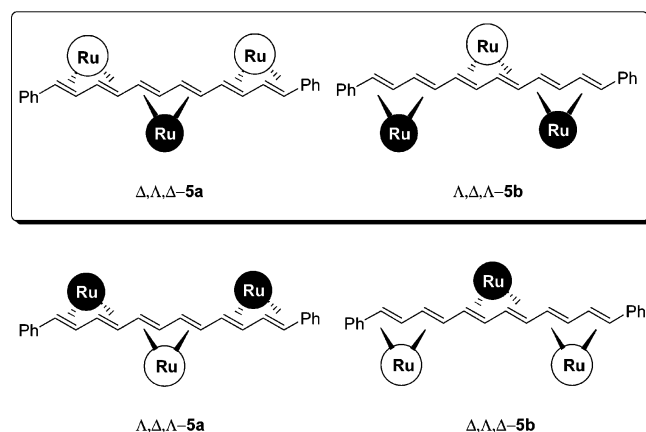
°C. The decrease in the intensity of H⁵ and H⁶ protons of **4** was found to be of first-order relative to complex **4**, and the activation parameter $\Delta G^\ddagger(25^\circ\text{C}) = 15.8 \pm 0.2$ kcal/mol was estimated. Such a movement of the ruthenium fragment may explain how ruthenium fragments coordinate to the polyene and cause the observed full metalation of polyenes.

Discussion

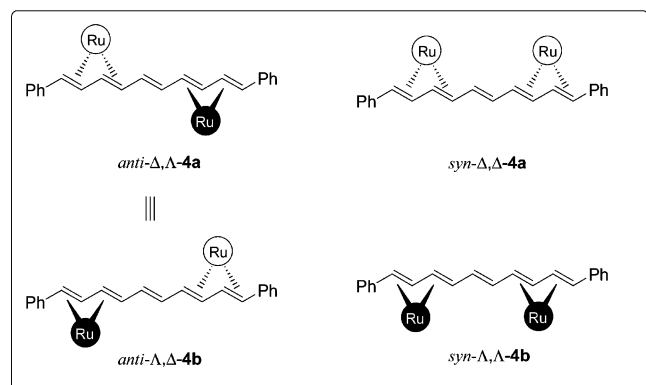
First, we discuss the stereochemistry of complexes **1**, **3**, and **5**, which have even numbers of olefinic parts. We have determined the crystal structures of **1** and **3**, which revealed that Δ -Ru(acac)₂ and Λ -Ru(acac)₂ fragments thermodynamically favored *re*- and *si*-faces, respectively, of the 1,4-diphenylbuta-1,3-diene and 1,8-diphenylocta-1,3,5,7-tetraene. There are 2⁴ possible structures for tetraene complex **3**, eight *anti* and eight *syn* isomers,¹⁶ of which *syn* isomers were ruled out due to the steric congestion of the *syn* isomers. Taking account of the symmetry of **3** (Scheme 2), *anti*- Δ,Δ -**3a**, *anti*- Λ,Λ -**3a**, *anti*- Δ,Λ -**3a**, and *anti*- Λ,Δ -**3a** equal the corresponding *anti*- Δ,Δ -**3b**, *anti*- Λ,Λ -**3b**, *anti*- Δ,Λ -**3b**, and *anti*- Λ,Δ -**3b** respectively. Moreover, *anti*- Δ,Δ -**3a** is the enantiomer of *anti*- Λ,Λ -**3b**, and *anti*- Λ,Λ -**3a** is that of *anti*- Δ,Δ -**3b**. Thus, the number of possible isomers for **3** is reduced to three magnetically nonequivalent isomers. Among them, according to the observed structure where Δ -Ru(acac)₂ and Λ -Ru(acac)₂ fragments preferred to coordinate to *re*- and *si*-faces of the diene, respectively,

(16) The total number, *N*, of the theoretically possible isomers for the polyene complexes can be expressed by equation, $N = 2^m$, where *m* is the number of C=C bonds of the polyene.

Scheme 3



Scheme 4



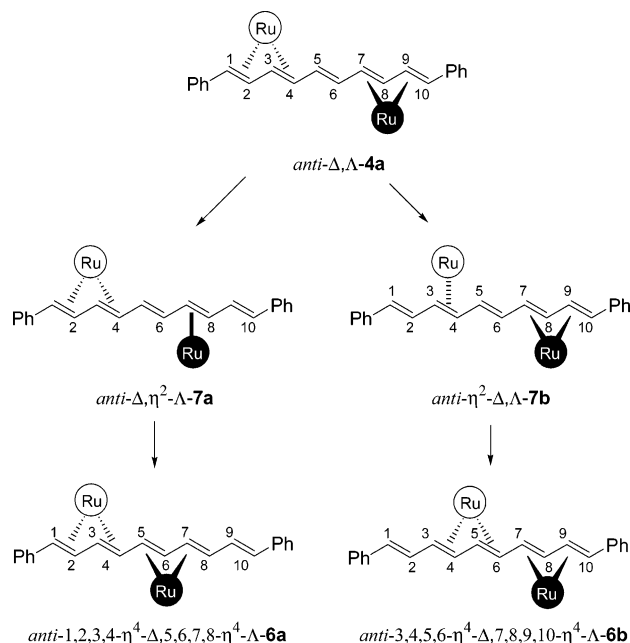
the structure of **3** was expected to be *anti*- Δ, Λ -**3a**, which is in accordance with the result of the X-ray analysis of **3**.

The structure of complex **5** is very complicated.¹⁶ All *syn,syn*-, *syn,anti*-, and *anti,syn*-isomers are ruled out because of the severe congestion among the ruthenium fragments. According to the preferential geometries of **1** and **3** (vide supra), complex **5** was assumed to be *anti,anti*- Δ, Λ, Δ -**5a** and *anti,anti*- $\Lambda, \Lambda, \Lambda$ -**5b** instead of the other diastereomer pair, *anti,anti*- Δ, Δ, Λ -**5a** and *anti,anti*- Δ, Λ, Δ -**5b** (Scheme 3).

After the completion of the irreversible isomerization from **4** to **6** at ambient temperature, we found that 20% of **4** always remained at any measured temperature. Possible structures for **4** are *anti*- Δ, Λ -**4a** and *syn*- Δ, Δ -**4a** and their enantiomers (*anti*- Λ, Δ -**4b** and *syn*- Λ, Λ -**4b**, respectively) because of the conformational preference (Scheme 4). All ruthenium fragments shown in Scheme 4 are magnetically equivalent since *anti*- Δ, Λ -**4a** (= *anti*- Λ, Δ -**4b**) has the inversion at the center of C(5)–C(6) in the pentaene backbone, and *syn*- Δ, Δ -**4a** and *syn*- Λ, Λ -**4b** have the C_2 -axis passing through the center of the pentaene ligand.

After migration of the Ru(acac)₂ fragment, it is reasonably assumed that the stereochemistry of complex **6** may adopt the *anti*-geometry. Scheme 5 shows the suprafacial movement of one of the two ruthenium fragments of *anti*- Δ, Λ -**4a**, whereby two magnetically equivalent *anti*- Δ, Λ -**6a** isomers resulted via η^2 -intermediates, depending on which ruthenium fragment moved. On the other hand, suprafacial migration of the ruthenium fragment on *syn*- Δ, Δ -**4a** and *syn*- Λ, Λ -**4b** did

Scheme 5



not proceed due to steric interaction between the two Ru(acac)₂. The observed ratio of the amounts of **4** and **6** suggests that 80% of the pentaene complex was *anti*- Δ, Λ -**4a** (= *anti*- Λ, Δ -**4b**), which was readily converted to *anti*- Δ, Λ -**6a** and *anti*- Δ, Λ -**6b** in chloroform, while the ruthenium fragment of *syn*- Δ, Δ -**4a** and *syn*- Λ, Λ -**4b** did not move, and thus these *syn*-isomers were observed as the minor product.

Conclusion

We demonstrated that the Ru(acac)₂ fragment coordinates in an η^4 -*s-trans* fashion to the diene unit of α, ω -diphenylpolyenes to afford the corresponding polyene complexes **1**–**6**. A noteworthy finding was that all diene units of the ligands were fully metalated. We also found that Δ -Ru(acac)₂ and Λ -Ru(acac)₂ could distinguish the *re*-face and *si*-face of the diene unit, respectively, as revealed by X-ray structural studies of **1** and **2** together with **3**. On the basis of such preferential geometry and bulkiness of Ru(acac)₂, we discussed the structures of pentaene and hexaene complexes: hexaene complex **5** was assumed to be an *anti,anti*-isomer, Δ, Λ, Δ -**5a**, and its enantiomer, Λ, Δ, Λ -**5b**. The structure of the pentaene complex with one free C=C bond was more complicated because there are two isomers, **4** and **6**, and furthermore, we found irreversible movement of one of two Ru(acac)₂ fragments of **4**, which yields **6**. We assigned **4** to be a mixture of *anti*- Δ, Λ -**4a** and *syn*-isomers, *syn*- Δ, Δ -**4a** and *syn*- Λ, Λ -**4b**. The Ru(acac)₂ fragment of *anti*- Δ, Λ -**4a** migrated to afford thermodynamically stable isomers, *anti*- Δ, Λ -**6a** and *anti*- Δ, Λ -**6b**, while *syn*- Δ, Δ -**4a** and *syn*- Λ, Λ -**4b** were not converted. We are currently interested in the full metalation of soluble polymers containing polyene units.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by standard Schlenk techniques under an argon atmosphere.

Toluene was dried over sodium benzophenone ketyl. Ethanol was distilled from magnesium ethoxide. 1,6-Diphenylhexa-1,3,5-triene was purchased from Aldrich Chemical Co., Inc. Ru(acac)₃,¹⁷ 1,10-diphenyldeca-1,3,5,7,9-pentaene,¹⁸ and 1,12-diphenyldodeca-1,3,5,7,9,11-hexaene¹⁸ were prepared according to the reported procedures. Zinc dust was activated by aqueous HCl, washed twice with acetone, and then dried under reduced pressure before use.

Nuclear magnetic resonance [¹H (400 MHz)] spectra were measured on a JEOL JNM-GSK400 spectrometer. Other spectra were recorded using the following instruments: IR, Jasco FT/IR-120 and 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 a TEXSAN computer system. Elemental analyses were performed using a Perkin-Elmer 2400 microanalyzer. All melting points were measured in sealed tubes and were not corrected.

Preparation of 2. 1,6-Diphenylhexa-1,3,5-triene (0.140 g, 0.600 mmol) and zinc dust (0.13 g) were added to a suspension of Ru(acac)₃ (0.242 g, 0.60 mmol) in ethanol (30 mL). The reaction mixture was refluxed for 12 h until the color became orange. The solvent was removed in vacuo, and then the residue was extracted with toluene (40 mL). Zinc dust and the Zn(acac)₂ formed were removed by centrifugation. The supernatant was concentrated and then cooled to -20 °C to give **2** (0.16 g, 51% yield) as a yellow-orange solid (mp 165–170 °C (dec)). Major isomer: ¹H NMR (CDCl₃, 30 °C): δ 1.56 (s, 3H), 1.91 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 3.86 (dd, 1H, H³, $J_{3,4}$ = 10.3 and $J_{2,3}$ = 6.9 Hz), 4.42 (d, 1H, H¹, $J_{1,2}$ = 11.0 Hz), 4.46 (dd, 1H, H², $J_{1,2}$ = 11.0 and $J_{2,3}$ = 6.9 Hz), 4.57 (dd, 1H, H⁴, $J_{4,5}$ = 10.7 and $J_{3,4}$ = 10.3 Hz), 5.37 (s, 1H), 5.44 (s, 1H), 6.31 (dd, 1H, H⁵, $J_{5,6}$ = 15.6 and $J_{4,5}$ = 10.7 Hz), 6.62 (d, 1H, H⁶, $J_{5,6}$ = 15.6 Hz), 7.13–7.23 (m, 10H, C₆H₅). Minor isomer: ¹H NMR (CDCl₃, 30 °C): δ 1.68 (s, 3H), 1.76 (s, 3H), 1.78 (s, 3H), 1.90 (s, 3H), 3.60 (dd, 1H, H³, $J_{3,4}$ = 10.3 and $J_{2,3}$ = 7.8 Hz), 4.30 (dd, 1H, H², $J_{1,2}$ = 11.5 and $J_{2,3}$ = 7.8 Hz), 4.70 (s, 1H), 5.20 (s, 1H), 5.35 (dd, 1H, H⁴, $J_{3,4}$ = 10.3 and $J_{4,5}$ = 10.7 Hz), 5.37 (d, 1H, H¹, $J_{1,2}$ = 11.5 Hz), 5.97 (dd, 1H, H⁵, $J_{5,6}$ = 15.6 and $J_{4,5}$ = 10.7 Hz), 6.76 (d, 1H, H⁶, $J_{5,6}$ = 15.6 Hz), 7.13–7.23 (m, 10H, C₆H₅). FAB-MS (N.B.A. matrix): m/z 532 (M⁺). IR (Nujol): ν (CO)/cm⁻¹ 1570 (m), 1550 (w), 1515 (s). UV/vis (CH₂Cl₂): $\lambda_{\max}$ 340 nm (ϵ = 2.1×10^4 M⁻¹ cm⁻¹). Anal. Calcd for C₂₈H₃₀O₄Ru: C, 63.25; H, 5.69. Found: C, 62.45; H, 5.73.

Preparation of 4. A reaction mixture of Ru(acac)₃ (0.224 g, 0.56 mmol), 1,10-diphenyldeca-1,3,5,7,9-pentaene (0.03 g, 0.10 mmol), and zinc dust (0.13 g) in ethanol (40 mL) was refluxed for 12 h. The color of the resulting solution became orange. After all volatiles were removed under reduced pressure, the residue was extracted with toluene (40 mL) to remove zinc dust and Zn(acac)₂. The extract was concentrated and cooled at -20 °C to give **4** (0.2 g, 81% yield) as a yellow-orange solid (mp 195–200 °C (dec)). ¹H NMR (C₆D₆, 30 °C): δ 1.57 (s, 6H), 1.71 (s, 6H), 1.76 (s, 6H), 2.25 (s, 6H), 3.96 (dd, 2H, H³ and H⁸, $J_{3,4}$ = $J_{7,8}$ = 11.0 and $J_{2,3}$ = $J_{8,9}$ = 7.3 Hz), 4.46 (dd, 2H, H² and H⁹, $J_{1,2}$ = $J_{9,10}$ = 10.7 and $J_{2,3}$ = $J_{8,9}$ = 7.3 Hz), 4.50 (dd, 2H, H⁴ and H⁷, $J_{3,4}$ = $J_{7,8}$ = 11.0 and $J_{4,5}$ = $J_{6,7}$ = 6.9 Hz), 4.58 (d, 2H, H¹ and H¹⁰, $J_{1,2}$ = $J_{9,10}$ = 10.7 Hz), 5.31 (s, 2H), 5.34 (s, 2H), 6.19 (dd, 2H, H⁵ and H⁶, $J_{5,6}$ = 10.7 and $J_{4,5}$ = $J_{6,7}$ = 6.9 Hz), 7.08–7.37 (m, 10H, C₆H₅). FAB-MS (N.B.A. matrix): m/z 833 (M⁺). IR (Nujol): ν (CO)/cm⁻¹ 1577 (m), 1514 (s). UV/vis (CH₂Cl₂): $\lambda_{\max}$ 343 nm (ϵ = 3.5×10^4 M⁻¹ cm⁻¹). Anal. Calcd for C₄₂H₄₈O₈Ru₂: C, 57.12; H, 5.48. Found: C, 57.31; H, 5.69.

Preparation of 5. 1,12-Diphenyldodeca-1,3,5,7,9,11-hexaene (0.16 g, 0.51 mmol) and zinc dust (0.36 g) were added to a mixture of Ru(acac)₃ (0.60 g, 1.50 mmol) in ethanol (30 mL).

Table 3. Crystal and Refinement Data for **1** and **2**

	1	2
formula	C ₂₆ H ₂₈ O ₄ Ru	C ₂₈ H ₃₀ O ₄ Ru
fw	505.57	531.61
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>a</i> (#14)	<i>P</i> 2 ₁ / <i>a</i> (#14)
<i>a</i> , Å	11.203(4)	11.864(3)
<i>b</i> , Å	11.469(3)	11.809(2)
<i>c</i> , Å	18.592(3)	18.611(4)
β , deg	92.52	103.49(1)
<i>Z</i>	4	4
<i>V</i> , Å ³	2386(1)	2535.6(9)
<i>d</i> _{calcd} , g cm ⁻³	1.407	1.392
radiation	Mo K α (λ = 0.71069 Å)	Mo K α (λ = 0.71069 Å)
reflms measd	<i>h</i> , <i>k</i> , $\pm$ l	<i>h</i> , <i>k</i> , $\pm$ l
cryst size, mm	0.2 $\times$ 0.2 $\times$ 0.3	0.2 $\times$ 0.2 $\times$ 0.2
abs coeff, cm ⁻¹	6.85	6.49
scan mode	ω -2 θ	ω -2 θ
temp, °C	20	20
2 θ _{max} , deg	55.0	55.0
no. of data collected	6046	6401
no. of unique data	5760	6116 (<i>R</i> _{int} = 0.021)
no. of observations	4361	3748
	(<i>I</i> > 1.5 σ (<i>I</i>))	(<i>I</i> > 3.0 σ (<i>I</i>))
no. of variables	392	298
<i>R</i> ^a	0.034	0.035
<i>R</i> _w ^b	0.025	0.038
GOF	2.59	1.54
Δ , e Å ⁻³	0.34	0.73 (max.)
	-0.62	-0.49 (min.)

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

The reaction mixture was refluxed for 12 h until the color became orange. The solvent was removed in vacuo, and then the residue was extracted with toluene (60 mL). The remaining zinc dust and Zn(acac)₂ were removed by centrifugation. The supernatant was concentrated and then cooled at -20 °C to yield **5** (0.10 g, 16% yield) as a yellow-orange solid (mp 125–130 °C (dec)). ¹H NMR (CDCl₃, 30 °C): δ 1.56 (s, 6H), 1.84 (s, 6H), 1.85 (s, 6H), 1.95 (s, 6H), 2.23 (s, 6H), 2.34 (s, 6H), 3.70 (m, 2H, H³ and H¹⁰), 3.87 (m, 2H, H⁶ and H⁷), 3.93 (m, 2H, H⁵ and H⁸), 4.00 (dd, 2H, H⁴ and H⁹, $J_{3,4}$ = $J_{9,10}$ = 10.3 Hz, $J_{4,5}$ = $J_{8,9}$ = 10.3 Hz), 4.38 (d, 2H, H¹ and H¹², $J_{1,2}$ = $J_{11,12}$ = 11.2 Hz), 4.41 (dd, 2H, H² and H¹¹, $J_{1,2}$ = $J_{11,12}$ = 11.2 and $J_{2,3}$ = $J_{10,11}$ = 7.3 Hz), 5.38 (s, 2H), 5.43 (s, 2H), 5.54 (s, 2H), 7.12–7.18 (m, 10H, C₆H₅). FAB-MS (N.B.A. matrix): m/z 1209 (M⁺). IR (Nujol): ν (CO)/cm⁻¹ 1571 (s), 1517 (s). UV/vis (CH₂Cl₂): $\lambda_{\max}$ 340 nm (ϵ = 4.3×10^4 M⁻¹ cm⁻¹). Elemental analysis did not give satisfactory data due to the presence of free ligands, which could not be removed by repeated recrystallization.

Kinetic Study of the Isomerization of 4 to 6. A sample of recrystallized pentaene complex **4** (6.6 mg, 7.4 mmol) in CDCl₃ (0.6 mL) was sealed in NMR tubes under argon atmosphere at room temperature. After the sample was prepared, isomerization of the pentaene complex was monitored by ¹H NMR at various temperatures (15, 18, 20, 21, 23, 25, and 27 °C). The value [*C*]_{*t*}, the concentration of **4** at reaction time *t*, was determined from the intensity of signals assignable to uncoordinated protons (= H⁵ and H⁶) to ruthenium in **4**. The new signals were observed and assigned to **6** together with the result of its COSY spectrum. The concentration of **6** was estimated from the intensity of the doublet (= H¹⁰) observed at 6.57 ppm. **6**: ¹H NMR (CDCl₃, 25 °C): δ 1.55 (s, 3H), 1.85 (s, 3H), 1.86 (s, 3H), 1.92 (s, 3H), 1.94 (s, 3H), 1.95 (s, 3H), 2.31 (s, 3H), 2.32 (s, 3H), 3.67 (dd, 1H, H³, $J_{2,3}$ = 7.8 and $J_{3,4}$ = 10.3 Hz), 3.78 (dd, 1H, H⁶, $J_{5,6}$ = 10.7 and $J_{6,7}$ = 7.8 Hz), 3.96 (dd, 1H, H⁵, $J_{4,5}$ = 10.3 and $J_{5,6}$ = 10.7 Hz), 3.97 (dd, 1H, H⁷, $J_{7,8}$ = 10.8 and $J_{6,7}$ = 7.8 Hz), 4.07 (dd, 1H, H⁴, $J_{4,5}$ = 10.3 and $J_{3,4}$ = 10.3 Hz), 4.32–4.43 (dd, 1H, H⁸, $J_{8,9}$ = 10.7 and $J_{7,8}$ = 10.3 Hz), 4.32–4.43 (d, 1H, H¹, $J_{1,2}$ = 10.3 Hz), 4.47 (dd, 1H, H², $J_{2,3}$ = 7.8 and $J_{1,2}$ = 10.3 Hz), 5.38 (s, 1H), 5.47 (s,

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1H), 5.50 (s, 1H), 5.52 (s, 1H), 6.26 (dd, 1H, H⁹, $J_{9,10}$ = 15.6 and $J_{8,9}$ = 10.7 Hz), 6.57 (d, 1H, H¹⁰, $J_{9,10}$ = 15.6 Hz), 7.08–7.37 (m, 10H, C₆H₅). Signals of H¹ and H⁸ overlapped each other and were assigned on the basis of the HH-COSY spectrum and the coupling constants between other protons.

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

The structures of **1** and **2** were determined by a direct method (SHELXS 86)¹⁹ and refined by the full-matrix least-squares method. In the refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and

calculated structure factor 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 of **1** and **2** were determined from a difference Fourier electron density map and refined anisotropically. All hydrogen atoms for each complex were placed at the 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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