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π-Conjugated α,ω-Diphenylpolyene Complexes of RuClCp* Fragment(s) in η^4-*s-cis* Conformation

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π-Conjugated polyene complexes of the general formula $(\mathrm{RuClCp}^*)_n$(polyene) [**2**: $n = 1$, polyene = 1,4-diphenylbuta-1,3-diene; **3**: $n = 1$, polyene = 1,6-diphenylhexa-1,3,5-triene; **4**: $n = 2$, polyene = 1,8-diphenylocta-1,3,5,7-tetraene; **5**: $n = 2$, polyene = 1,10-diphenyldeca-1,3,5,7,9-pentaene; **6**: $n = 3$, polyene = 1,12-diphenyldodeca-1,3,5,7,9,11-hexaene], in which each ruthenium(II) atom has Cp* (Cp* = η^5-C_5Me_5) and chlorido ligands, were prepared by treating $[\mathrm{Ru}(\mu_3\text{-Cl})\mathrm{Cp}^*]_4$ (**1**) with the corresponding α,ω-diphenylpolyenes. All diene units of the complexes were fully metalated by the coordination of "RuClCp*" fragments in an η^4-*s-cis* conformation.

Introduction

One-dimensional π-conjugated polyenes are excellent supporting ligands to which plural transition metals can coordinate, and their metal complexes are expected to show unique properties on the basis of an extended pπ–dπ conjugated organometallic system.[1] Their physical properties are thus controlled by not only the number of transition metals bound to the polyene ligand but also their coordination features such as nuclearity (mono-,[2,3] di-,[4] or polynuclear[5]), stereochemistry (*syn* and *anti* for polynuclear complexes), and fluxionality[6,7] (metal migration on a polyene). Moreover, ancillary ligands on a metal center also play an important role in controlling the structure and properties of π-conjugated polyene complexes. We have recently reported the systematic preparation of α,ω-diphenylpolyene complexes bearing $\mathrm{Ru(acac)_2}$ (acac = acetylacetonato) fragments, which coordinate to all diene units of the polyene in an η^4-*s-trans* fashion,[8a] resulting in the full metalation of all diene units of the polyenes. In contrast, ruthenium fragments with Cp* (Cp* = C_5Me_5) and chlorido ligands prefer to coordinate to a diene moiety of diene and tetraene in an η^4-*s-cis* fashion revealed by our previous work.[8b] The selectivity of coordination mode originating from the difference of ancillary ligands on a ruthenium center has attracted interest. Furthermore, "RuClCp*" fragments as well as "$\mathrm{Ru(acac)_2}$"[8a] and "$\mathrm{Fe(CO)_3}$"[7] fragments are also expected to move on a π-conjugated polyene with an odd number of olefinic parts such as triene and pentaene. As an extension of our continuing interest in this area, we have investigated the complexation of the "RuClCp*" fragment with longer polyenes. Here, we report the synthesis of a series of α,ω-diphenylpolyene complexes (polyene = di-, tri-, tetra-, penta-, and hexaene) bearing RuClCp* fragments and their structural features.

Results and Discussion

The reaction of α,ω-diphenylpolyenes with $[\mathrm{Ru}(\mu_3\text{-Cl})\mathrm{Cp}^*]_4$ (**1**)[2g] in THF or dichloromethane at room temperature gave the corresponding chlorido(η^5-pentamethylcyclopentadienyl)ruthenium(II) complexes of the general formula $(\mathrm{RuClCp}^*)_n$(polyene) [**2**: $n = 1$, polyene = 1,4-diphenylbuta-1,3-diene; **3**: $n = 1$, polyene = 1,6-diphenylhexa-1,3,5-triene; **4**: $n = 2$, polyene = 1,8-diphenylocta-1,3,5,7-tetraene; **5**: $n = 2$, polyene = 1,10-diphenyldeca-1,3,5,7,9-pentaene; **6**: $n = 3$, polyene = 1,12-diphenyldodeca-1,3,5,7,9,11-hexaene] in modest yields [Equation (1)]. Among them, the diene and tetraene complexes **2** and **4** had previously been prepared and characterized.[8b] Both complexes are stable to air and moisture in the solid state, but are not stable in solution. Complexes **3**, **5**, and **6** are soluble in dichloromethane and chloroform, and are slightly soluble in THF. The treatment of **1** with longer polyenes such as 1,14-diphenyltetradeca-1,3,5,7,9,11,13-heptaene and 1,16-diphenylhexadeca-1,3,5,7,9,11,13,15-octaene did not yield any products because of the low solubility of heptaene and octaene ligands in any common organic solvent.

In the obtained complexes, RuClCp* fragments coordinated in an η^4-*s-cis* fashion to all diene units of the polyenes. The ^{1}H NMR spectra of all complexes (except **2**) showed signals of the outer protons of coordinated diene

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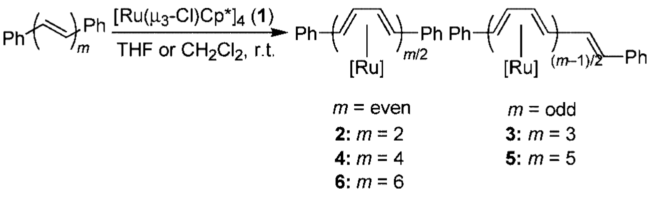


(1)

units in the range of $\delta = 2.5$–4.0 ppm. Siganls of the inner protons of the *s-cis* diene moieties are observed at $\delta \approx 5$ ppm, with a smaller coupling constant ($^3J = 5.9$ Hz),[2] in sharp contrast to those ($^3J = 7$–8 Hz) observed for η4-*s-trans*-diene[3] complexes of Ru(acac)$_2$ fragments.

The conformation of a diene moiety around a ruthenium center can be explained by the electron influence of ancillary ligands.[1b] Some (diene)ruthenium complexes, Ru(acac)$_2$(η4-1,3-diene),[3f] TpRuCl(η4-1,3-diene),[3h] and [Ru(NH$_3$)$_4$(η4-1,3-diene)]$^{2+}$,[3i] prefer the *s-trans* mode, presumably because the electronic deficiency around the ruthenium center of each fragment, as compared with the "RuClCp*" fragment, is compensated for by electron donation from the *s-trans*-diene ligand. In addition, the overall stereochemistry at a ruthenium center may influence the conformation mode. The above *s-trans*-diene complexes have a hexacoordinate octahedral structure when the *s-trans*-diene moiety is regarded as a bidentate chelating ligand. In the case of RuClCp*(η4-1,3-diene), the regular octahedral structure of the Ru^{II} complex is deviated by a bulky tridentate Cp* ligand. Thus, the diene moiety of the polyene complexes prefers the *s-cis* coordination.

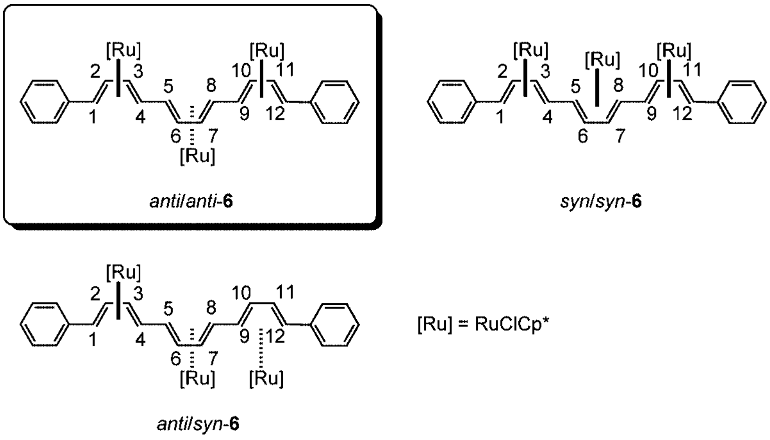
UV/Vis spectroscopic data of **2**–**6** together with those of η4-*s-trans*-polyene complexes with Ru(acac)$_2$ fragments[8a] are summarized in Table 1. The absorption maxima of **2**–**6** shift to a longer wavelength as the number of diene units of the polyene ligand increases, indicating that the π-conjugated system along the polyene chain is kept even after the dπ orbital of the RuClCp* fragment is incorporated in the pπ orbital of the polyene, consistent with the results of the X-ray analysis of **4**.[8b] In contrast, we observed that η4-*s-trans*-polyene complexes containing Ru(acac)$_2$ fragments have almost the same absorption maxima because their π-conjugation systems are separated into individual diene units due to the structural deformation of ruthenium-coordinated diene units. These UV/Vis data also suggest that ancillary ligands (Cp* or acac) on a ruthenium center can control not only their structural shape, such as the metal coordination mode (*s-cis* or *s-trans* for diene complexation), but also the planarity of the polyene backbone.

Table 1. UV/Vis spectroscopic data of (polyene)ruthenium complexes, [Ru](α,ω-diphenylpolyene) in CH$_2$Cl$_2$.

Diphenylpolyene	λ_{max}/nm (ε/M cm^{-1})	
	[Ru] = RuClCp*	[Ru] = Ru(acac)$_2$
Butadiene	481 (5900) (**2**)	325 (1300)[a]
Hexatriene	492 (6800) (**3**)	340 (21000)[b]
Octatetraene	518 (11400) (**4**)	340 (2600)[a]
Decapentaene	525 (16500) (**5**)	343 (35000)[b]
Dodecahexaene	525 (–) (**6**)[c]	340 (43000)[b]

[a] Ref.[8b] [b] Ref.[8a] [c] Because of the low solubility of **6**, we could not estimate the ε value.

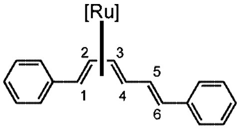
The ^{1}H NMR spectra of **2**, **4**, and **6** displayed no peaks assignable to the uncoordinated olefinic protons in the range of $\delta = 6$–7 ppm, indicating that polyenes with an even number of olefinic parts are fully metalated.[8] For **4**, we attempted to carry out the reaction of a tetraene ligand with 1 equiv. of **1** to obtain a mononuclear complex; however, no partly metalated olefinic parts with one ruthenium fragment was observed, and a mixture of **4** and a free tetraene was detected by NMR analysis. Likewise, the reaction of **1** with a hexaene gave **6**, without any complexes, having one or two ruthenium fragments. For the multinuclear complexes **4** and **6**, there are several possible *syn* and *anti* isomers owing to the relative face selection of sequential metal coordination across the polyene ligand. For the tetraene complex **4**, an *anti* structure of two RuClCp* fragments coordinated to a tetraene has been revealed by X-ray analysis.[8b] The ^{1}H NMR spectrum of the trinuclear hexaene complex **6** in CDCl$_3$ showed only one set of six olefinic protons together with two methyl protons (1:2 ratio) of Cp*



Scheme 1.

ligands, suggesting that **6** may have a C_2 axis or a mirror plane passing through the central ruthenium atom and the center of the hexaene ligand. For **6**, four isomers are possible, which are categorized into three types: *syn*/*syn*-, *anti*/*anti*-, and *anti*/*syn*- (= *syn*/*anti*-) **-6**, as depicted in Scheme 1. On the basis of the ^{1}H NMR spectrum of **6**, the structurally unsymmetrical isomer *anti*/*syn*-**6** is excluded. Furthermore, *syn*/*syn*-**6** is also ruled out because of steric repulsion among the three bulky RuClCp* fragments. Thus, it is reasonably conceivable that **6** has an *anti*/*anti* structure.

In contrast to those of **4** and **6**, the ^{1}H NMR spectrum of the triene complex **3** exhibited six signals of magnetically nonequivalent nuclei: four peaks in the range of δ = 3.3–5.4 ppm were from olefinic protons of the diene part bound to a ruthenium atom and the other two signals observed at δ ≈ 6.5 ppm were assignable to noncoordinating olefin protons. The RuClCp* fragment coordinated in an *s-cis* fashion to a diene part of the triene, as judged from a typical coupling constant (^3J = 5.9 Hz) between the inner protons H^2 and H^3 (signals observed at δ = 5.28 and 4.90 ppm).[2] The coupling constants $J_{4,5}$ (10.3 Hz) and $J_{5,6}$ (15.6 Hz) further indicated that the C(3)–C(4)–C(5)–C(6) sequence is *s-trans*.



3

[Ru] = RuClCp*

The dinuclear pentaene complex **5** was isolated as a mixture of two isomers: **5a** (major, 90%) and **5b** (minor, 10%). In the 2D COSY and NOESY spectra of **5** (Figures 1 and 2), 10 signals of magnetically nonequivalent nuclei assignable to the major isomer **5a** revealed that two ruthenium fragments coordinated to two neighboring diene moieties (1,2,3,4-η^4 and 5,6,7,8-η^4 coordination); five peaks due to the minor isomer **5b** indicated that two ruthenium fragments coordinated at separated positions (1,2,3,4-η^4 and 7,8,9,10-η^4 coordination).

There are four (= 2^2) possible structures of complex **5**: two *syn* and two *anti* isomers are schematically depicted in Scheme 2. When the pentaene ligand reacted with **1**, it is assumed that there were two partly metalated intermediates (1,2,3,4-η^4-**7** and 3,4,5,6-η^4-**7**). For the latter intermediate,

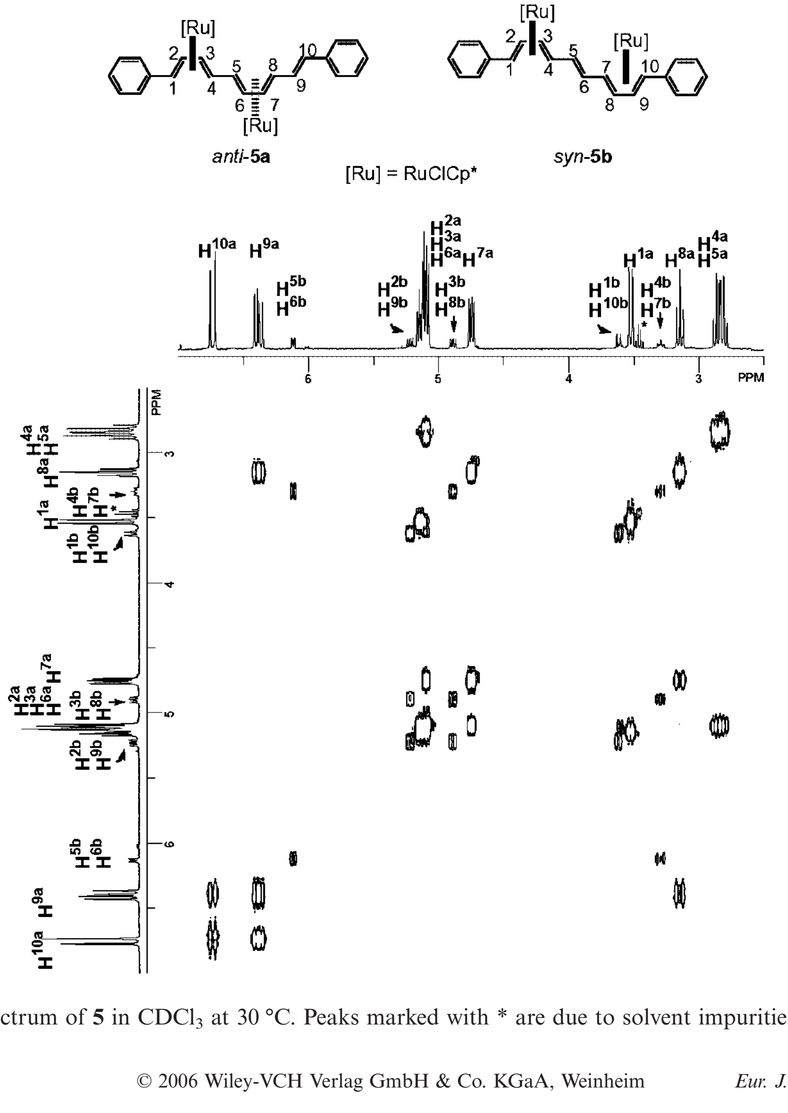


Figure 1. The 2D COSY spectrum of **5** in CDCl$_3$ at 30 °C. Peaks marked with * are due to solvent impurities.

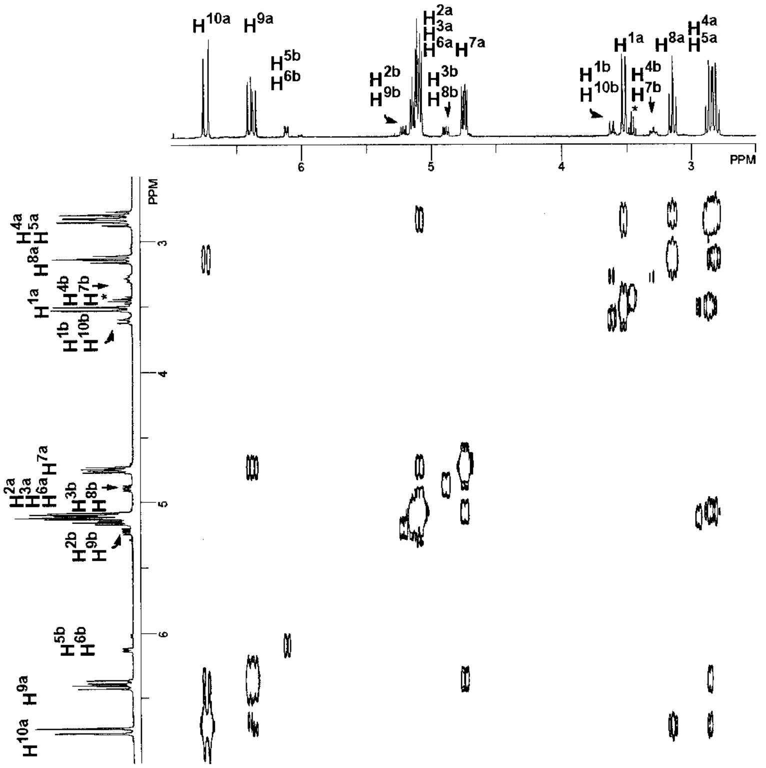
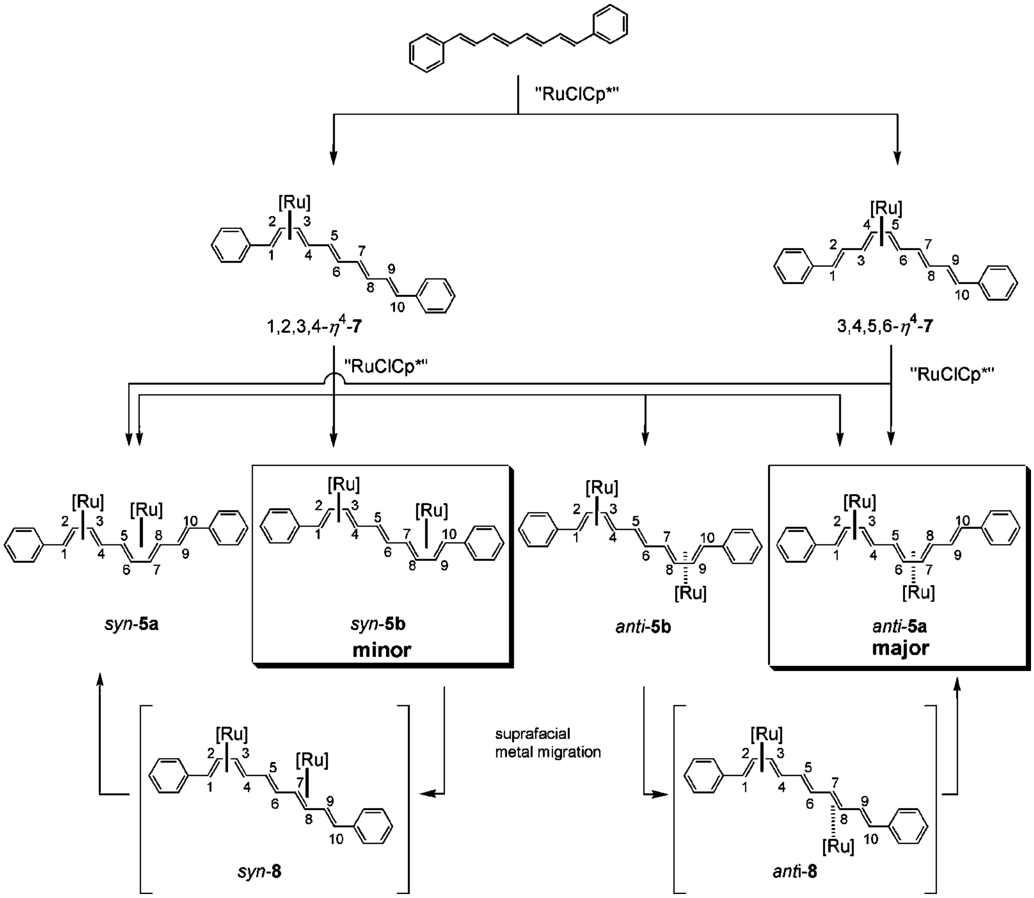


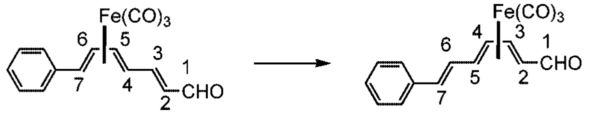
Figure 2. The 2D NOESY spectrum of **5** in $CDCl_3$ at 30 °C. Peaks marked with * are due to solvent impurities.



Scheme 2.

one diene part [C(7)–C(8)–C(9)–C(10)] remained intact and was applicable to the coordination of another RuClCp* fragment, giving *anti*-**5a** and *syn*-**5a**. On the other hand, the former one has a triene part, to which the coordination of another ruthenium fragment affords four possible isomers (*anti*-**5a**, *syn*-**5a**, *anti*-**5b**, and *syn*-**5b**). Among these isomers, *syn*-**5a** was ruled out because of steric repulsion between the two Cp* rings. Thus, the structure of the major isomer **5a** was concluded to be *anti*-**5a**. In contrast, from the ^{1}H NMR spectrum of **5b**, the stereochemistry of the minor product **5b** could not be determined because two possible isomers (*anti*-**5b** and *syn*-**5b**) displayed the same signals (magnetically equivalent nuclei) due to the inversion at the center of C(5)–C(6) in the pentaene ligand for *anti*-**5b**, and the C_2 axis passing through the center of the pentaene backbone for *syn*-**5b**.[8a]

The minor product **5b** remained even at elevated temperatures; the percentage of **5b** did not change on heating the chloroform solution of **5**, indicating that either *syn*-**5b** or *anti*-**5b** is thermodynamically stable. As shown in Scheme 2, the major isomer *anti*-**5a** was also produced by the migration of an RuClCp* fragment of *anti*-**5b** via the η^2-intermediate *anti*-**8**, based on the assumption that a ruthenium fragment suprafacially moved over the pentaene ligand. On the other hand, the suprafacial migration of a ruthenium fragment on *syn*-**5b** did not proceed via *syn*-**8**, because of the steric congestion between two RuClCp* fragments of *syn*-**5a**. Thus, *syn*-**5b** was observed as the minor product and its percentage did not change. Scheme 3 depicts an example of metal migration on a polyene ligand for a trienal complex of the iron compound Fe(CO)$_3$(7-phenyl-2,4,6-heptatrienal). An isomer with an iron fragment at neighboring positions of a phenyl group has been isomerized to another isomer with an iron fragment at neighboring positions of an electron-withdrawing formyl group through the migration of a tricarbonyliron fragment over a trienal ligand.[7b] Accordingly, it is concluded that the treatment of **1** with a pentaene ligand finally gives *anti*-**5a** and *syn*-**5b** as major and minor products, respectively.



Scheme 3.

Conclusions

We demonstrated that the ruthenium fragment RuClCp* coordinates in an *s-cis* fashion to α,ω-diphenylpolyenes to afford the corresponding polyene complexes **2**–**6**, in sharp contrast to the case of η^4-*s-trans*-polyene complexes with Ru(acac)$_2$ fragments. All diene units were fully metalated with RuClCp* fragments. We also found that the coordination of RuClCp* fragments maintains a long π-conjugation system along the polyene chain in comparison with η^4-*s-trans*-polyene complexes with Ru(acac)$_2$ fragments, as revealed by UV/Vis spectroscopy. We also discussed the structures of pentaene and hexaene complexes on the basis of the bulkiness of RuClCp* moieties: the hexaene complex **6** was assumed to have *anti*/*anti* geometry. The pentaene complex **5** was isolated as a mixture of two isomers: **5a** (major) and **5b** (minor). The RuClCp* fragment of one minor isomer, *anti*-**5b**, suprafacially moved over the pentaene backbone to afford the major isomer *anti*-**5a**, and the other isomer, *syn*-**5b**, remained as the minor product. This supports our previous conclusion that ancillary ligands (Cp* or acac) on a ruthenium center play an important role in controlling their structural shape, such as the metal coordination mode (*s-cis* or *s-trans* for diene complexation) and planarity of the polyene backbone.

Experimental Section

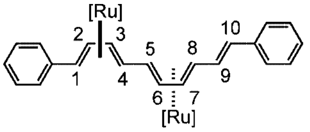
General Procedure: All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk techniques under argon. THF, hexane, toluene, and diethyl ether were dried and deoxygenated by distillation from sodium/benzophenone ketyl under argon. Dichloromethane was purified by distillation after drying with CaH$_2$. 1,6-Diphenyl-1,3,5-hexatriene was purchased from Aldrich Chemical Co., Inc.; [Ru(μ_3-Cl)Cp*]$_4$,[2g] 1,10-diphenyl-1,3,5,7,9-decapentaene,[9] and 1,12-diphenyl-1,3,5,7,9,11-dodecahexaene[9] were prepared according to literature procedures. The preparation of **2** and **4** has already been reported.[8b] NMR [^{1}H (400 MHz)] spectra were measured using a JEOL JNM-GSK400 spectrometer. The assignments of the ^{1}H NMR peaks of some complexes were aided by 2D COSY and NOESY spectra. Other spectra were recorded using the following instruments: IR: Jasco FTIR-120 and Hitachi 295; low- and high-resolution MS: JEOL SX-102. UV/Vis: Jasco Ubest-30 and Shimadzu UV-265FS. Elemental analyses were performed with a Perkin–Elmer 2400 instrument at the Faculty of Engineering Science, Osaka University. All melting points were measured in sealed tubes and are not corrected.

Synthetic Procedures

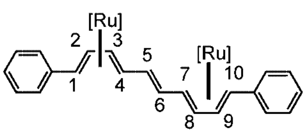
Complex 3: 1,6-Diphenyl-1,3,5-hexatriene (0.092 g, 0.40 mmol) was added to a solution of [Ru(μ_3-Cl)Cp*]$_4$ (**1**) (0.120 g, 0.11 mmol) in THF (50 mL) at 25 °C. The color of the reaction mixture turned bright red, and then red solids precipitated. After the reaction mixture was stirred for 3 h, the red precipitates were collected and washed with hexane (5 mL). Recrystallization from dichloromethane afforded **3** (0.12 g, 60% yield) as red microcrystals, m.p. 220–230 °C (dec.). ^{1}H NMR (CDCl$_3$, 30 °C): δ = 7.17–7.52 (m, 10 H, C_6H_5), 6.82 (d, $J_{5,6}$ = 15.6 Hz, 1 H, H^6), 6.44 (dd, $J_{4,5}$ = 10.3 Hz, 1 H, H^5), 5.28 (dd, $J_{1,2}$ = 10.7 and $J_{2,3}$ = 5.9 Hz, 1 H, H^2), 4.90 (dd, $J_{3,4}$ = 10.7 Hz, 1 H, H^3), 3.68 (d, 1 H, H^1), 3.40 (dd, 1 H, H^4), 1.36 (s, 15 H, C_5Me_5) ppm. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) = 492 nm (6800 L mol^{-1} cm^{-1}). MS (FAB): *m*/*z* = 504 [M$^+$]. C$_{28}$H$_{31}$ClRu (504.07): calcd. C 66.72, H 6.20; found C 66.43, H 6.30.

Complex 5: 1,10-Diphenyl-1,3,5,7,9-decapentaene (0.170 g, 0.60 mmol) was added to a dichloromethane (50 mL) solution of **1** (0.350 g, 0.32 mmol), and the reaction mixture was stirred at room temperature for 3 h. After removing insoluble impurities by centrifugation, the resulting red solution was concentrated to approximately 5 mL and kept at –20 °C, affording **5** (0.26 g, 52% yield) as red microcrystals, m.p. 190–200 °C (dec.). Major isomer (*anti*-**5a**): ^{1}H NMR (CDCl$_3$, 30 °C): δ = 7.10–7.50 (m, 10 H, C_6H_5), 6.74 (d,

$J_{9,10}$ = 15.6 Hz, 1 H, H^{10}), 6.38 (dd, $J_{8,9}$ = 10.3 Hz, 1 H, H^9), 5.15 (dd, $J_{1,2}$ = 10.3 and $J_{2,3}$ = 5.9 Hz, 1 H, H^2), 5.14 (dd, $J_{3,4}$ = 9.3 Hz, 1 H, H^3), 5.10 (dd, $J_{6,7}$ = 5.9 and $J_{5,6}$ = 9.3 Hz, 1 H, H^6), 4.75 (dd, $J_{7,8}$ = 10.3 Hz, 1 H, H^7), 3.52 (d, 1 H, H^1), 3.15 (t, 1 H, H^8), 2.85 (dd, $J_{4,5}$ = 10.3 Hz, 1 H, H^4), 2.81 (dd, 1 H, H^5), 1.53 (s, 15 H, C_5Me_5), 1.31 (s, 15 H, C_5Me_5) ppm. Minor isomer (*syn*-**5b**): ^{1}H NMR ($CDCl_3$, 30 °C): δ = 7.10–7.50 (m, 10 H, C_6H_5), 6.12 (m, 2 H, H^5 and H^6), 5.21 (dd, $J_{2,3}$ and $J_{8,9}$ = 5.9, $J_{1,2}$ and $J_{9,10}$ = 10.7 Hz, 2 H, H^2 and H^9), 4.89 (dd, $J_{3,4}$ and $J_{7,8}$ = 10.3 Hz, 2 H, H^3 and H^8), 3.62 (d, 2 H, H^1 and H^{10}), 3.15 (m, 2 H, H^4 and H^7), 1.32 (s, 30 H, C_5Me_5) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 525 nm (16000 L mol^{-1} cm^{-1}). MS (FAB): *m*/*z* = 556 [M^+ – RuCp*Cl]. $C_{42}H_{50}Cl_2Ru_2$ (827.89): calcd. C 60.92, H 6.09; found: C 60.44, H 5.90.



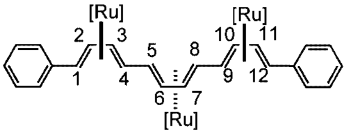
anti-**5a**



syn-**5b**

[Ru] = RuClCp*

Complex 6: A reaction mixture of **1** (0.0820 g, 0.075 mmol) and 1,12-diphenyl-1,3,5,7,9,11-dodecahexaene (0.0310 g, 0.10 mmol) in CH_2Cl_2 (30 mL) was stirred at 25 °C for 3 h to give a red precipitate. The precipitate was filtered and then washed with hexane (5 mL). Recrystallization from dichloromethane afforded **6** (0.043 g, 38% yield) as red microcrystals, m.p. 195–200 °C (dec.). ^{1}H NMR ($CDCl_3$, 30 °C): δ = 7.12–7.46 (m, 10 H, C_6H_5), 5.15 (dd, 2 H, H^2 and H^{11}), 5.09 (dd, $J_{2,3}$ and $J_{10,11}$ = 5.9 Hz, 2 H, H^3 and H^{10}), 5.01 (dd, $J_{6,7}$ = 4.4 and $J_{5,6}$ and $J_{7,8}$ = 9.3 Hz, 2 H, H^6 and H^7), 3.53 (d, $J_{1,2}$ and $J_{11,12}$ = 10.7 Hz, 2 H, H^1 and H^{12}), 2.91 (dd, $J_{3,4}$ and $J_{9,10}$ = 10.3 and $J_{4,5}$ and $J_{8,9}$ = 9.8 Hz, 2 H, H^4 and H^9), 2.69 (dd, 2 H, H^5 and H^8), 1.52 (s, 15 H, C_5Me_5), 1.32 (s, 30 H, C_5Me_5) ppm. UV/Vis (CH_2Cl_2): λ_{max} = 525 nm. MS (FAB): *m*/*z* = 547 [M^+ – 2 Cp*RuCl – Cl]. The low solubilities of both the complex and 1,12-diphenyl-1,3,5,7,9,11-dodecahexaene prevented the separation of the polyene by repeated crystallizations, and an elemental analysis of the complexes could not be performed.



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[Ru] = RuClCp*

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