Synthesis of Mono-, Di-, and Triruthenium(0) Complexes Having a Triphenylene Ligand†

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A series of mono-, di-, and triruthenium(0) complexes containing a triphenylene ligand, [Ru(η^4-1,5-COD)]$_n$(η^{6n}-triphenylene) (n = 1 (**2**), 2 (**3**), 3 (**6**)) have been prepared by the ligand exchange reaction of Ru(η^4-1,5-COD)(η^6-naphthalene) (**1**) with triphenylene, reduction of Ru(acac)$_2$(η^4-1,5-COD) (**4**) with sodium/triphenylene, or hydrogenolysis of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**5**) in the presence of triphenylene. These triphenylene complexes are interconvertible with each other by addition of a "Ru(η^4-1,5-COD)" fragment or free triphenylene.

Introduction

The (η^6-arene)ruthenium complexes have been widely used as precursors for organoruthenium complexes,[1,2] organometallic materials,[3] and medicinal reagents.[4] They have also been particularly employed in a variety of catalyses such as regioselective olefin dimerization,[5] hydroamination,[6] hydrogenation[7] and transfer hydrogenation,[8] the Diels−Alder reaction,[9] and ring-opening metathesis polymerization.[10] Among (η^6-arene)ruthenium complexes, syntheses of ruthenium(0) complexes with polycyclic aromatic hydrocarbons have been far less explored than those of ruthenium(II),[11] except for (η^6-naphthalene)-ruthenium(0) complexes.[12,13] We have recently reported the synthesis and reactions of tricyclic arene complexes such as phenanthrene, anthracene, and 9,10-dihydroanthracene formulated as Ru(η^4-1,5-COD)(η^6-tricyclic arene).[14] In this article, it was suggested that the uncoordinated part of the tricyclic arenes still has aromatic character for phenanthrene and 9,10-dihydroanthracene. Thus, the uncoordinated aromatic rings in some polycyclic ligand may provide another 6π site for coordination of the second metal fragment, giving multinuclear complexes. This working hypothesis prompted us to explore the synthesis of multinuclear ruthenium(0) complexes of a polycyclic aromatic ligand, which would provide new routes for two-dimensional accumulation and alignment of ruthenium metals, though one-dimensional alignments of various metal fragments have been extensively studied for development of new materials in recent years.[15] Similar pioneering studies on polycyclic aromatic complexes have mainly been developed by use of transition-metal carbonyl complexes,[1,16] but multinuclear polycyclic aromatic complexes with labile "Ru(η^4-1,5-COD)" fragments are unprecedented to our knowledge.

In this paper we wish to report the synthesis and reactions of mono-, di-, and trinuclear ruthenium(0) complexes having a triphenylene ligand.

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† Abbreviations used in this text: COD = cyclooctadiene (C_8H_{12}); COT = cyclooctatriene (C_8H_{10}); acac = acetylacetonato (2,4-pentanedionato, $C_5H_7O_2$).

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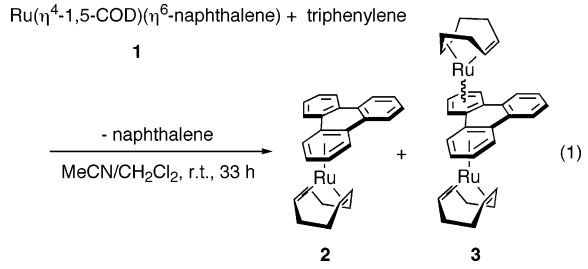
Results and Discussion

Arene Exchange Reaction. First, the arene exchange reaction of Ru(η^4-1,5-COD)(η^6-naphthalene) (**1**) with an aromatic compound in the presence of MeCN was applied for the synthesis of (triphenylene)ruthenium(0) complexes.[2j] The reaction of **1** with 1 equiv of triphenylene in MeCN/CH_2Cl_2 (1/30 v/v) at room temperature for 33 h resulted in the formation of a mixture of Ru(η^4-1,5-COD)(η^6-triphenylene) (**2**) and [Ru(η^4-1,5-COD)]$_2$-(μ^2-η^6:η^6-triphenylene) (**3**) in 45 and 27% yields, respectively (eq 1). When 4 equiv of triphenylene/equiv of **1** was used in



MeCN/CH_2Cl_2 under comparable conditions, **2** was selectively formed in quantitative yield.

On the other hand, when **1** was treated with 0.3 equiv of triphenylene in MeCN/CH_2Cl_2 at room temperature, selective precipitation of a yellow powder of **3** took place. Removal of the supernatant followed by washing of the precipitate with MeCN and recrystallization from cold CH_2Cl_2 (−80 °C) gave orange crystals of pure **3** in 21% yield based on triphenylene. These results show that the **1**/triphenylene ratio is a key factor in the preferential formation of **3**. Formation of the dinuclear complex **3** demonstrates the uncoordinated aromatic ring in a polycyclic arene complex to have sufficient aromaticity for coordination of an extra Ru moiety.

Complexes **2** and **3** were characterized by ^{1}H NMR and ^{1}H−^{1}H COSY, and **2** was also characterized by an X-ray analysis. The molecular structure of **2** is depicted in Figure 1 and is found to have a η^6-triphenylene ligand on the Ru(η^4-1,5-COD) fragment with C_s symmetry. The selected bond distances are listed in Table 1.

The overall structure of **2** is similar to that of Cr(CO)$_3$(η^6-triphenylene).[17] The triphenylene ligand is not distorted from planarity. For example, the greatest deviation from the least-squares plane in **2** occurs for C2 and C3, which lie −0.101(9) and 0.056(8) Å, respectively, from the plane. The bond distances found in the uncoordinated benzo rings in **2** are comparable to those in free triphenylene,[18] suggesting that they are still expected to have enough aromaticity. The ^{1}H NMR spectrum of **2** shows a multiplet at δ 1.62 (8H) and a broad singlet at δ 3.0 (4H) assignable to the methylene and methine protons in the 1,5-COD ligand. An AA′BB′ pattern at δ 5.5 (2H) and 6.1 (2H) is due to the coordinated aromatic protons, suggesting C_s symmetry in **2**. Three sets of signals were observed in the aromatic region at δ 7.6 (m, 4H), 8.09 (dd, 2H), and 8.61 (dd, 2H), assigned as aromatic protons in the uncoordinated ring. These data are consistent with the mononuclear structure of **2**. In the ^{1}H NMR spectrum of **3**, a broad multiplet at δ 1.7 (16H) and two multiplets at δ 3.02 (4H) and 3.13 (4H) are assignable to the COD moiety, suggesting the presence of two 1,5-COD ligands. Two doublets at δ 5.23 (2H) and 5.64 (2H) and two triplets at δ 6.06 (2H) and 6.12 (2H) are assigned as coordinated aromatic protons, and an AA′BB′ pattern at δ 7.60 (2H) and 8.09 (2H) is due to the aromatic protons in the uncoordinated ring. All these data are also consistent with the dinuclear structure of **3**, though it is not clear whether the two Ru(η^4-1,5-COD) fragments are on the same side (syn) or the opposite side (anti). It is notable that though pioneering examples of bimetallic complexes of π-conjugated polycyclic arenes having η^6:η^6,[19] η^6:η^5,[20] η^6:η^4,[21] η^4:η^4,[22] η^3:η^3,[23] or η^2:η^2 bonding have been documented,[24,25] those of ruthenium(0) are quite limited, with the exception of *anti*-[Ru(η^4-1,5-COD)][RuL(η^4-1,5-COD)]-(μ^2-η^6:η^4-naphthalene) (L = PEt_3, $P(OMe)_3$).[21d]

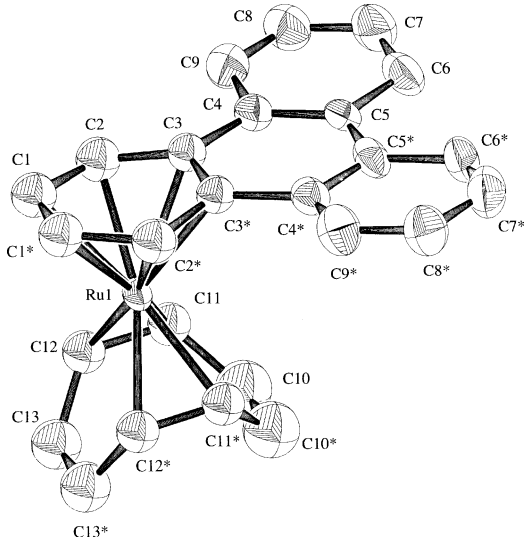


Figure 1. ORTEP drawing of Ru(η^4-1,5-COD)(η^6-triphenylene) (**2**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability. The molecule has C_s symmetry, and atoms designated with an asterisk were generated by the symmetrical operation. No distinguishable disorder was observed.

Table 1. Selected Bond Distances (Å) for 2

Ru(1)−C(1)	2.25(1)	Ru(1)−C(2)	2.18(1)
Ru(1)−C(3)	2.298(10)	C(1)−C(1)*	1.37(2)
C(1)−C(2)	1.45(2)	C(2)−C(3)	1.41(1)
C(3)−C(3)*	1.45(2)	C(3)−C(4)	1.48(1)
C(4)−C(5)	1.40(1)	C(4)−C(9)	1.39(2)
C(5)−C(5)*	1.47(2)	C(5)−C(6)	1.41(1)
C(6)−C(7)	1.37(2)	C(7)−C(8)	1.36(2)
C(8)−C(9)	1.36(2)		

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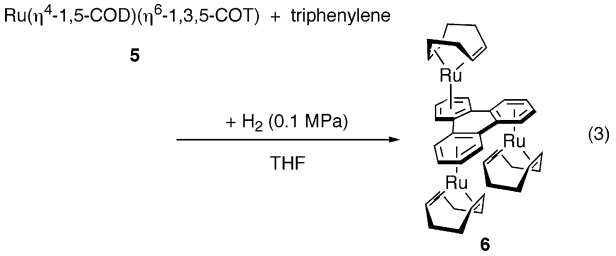
Two-Electron Reduction of the Ru(II) Complex with Sodium/Triphenylene. Second, two-electron reduction of Ru(acac)$_2$(η^4-1,5-COD) (**4**) with twice the amount of radical anions of aromatic compounds is used for the preparation of (arene)ruthenium(0) complexes.[12] The treatment of **4** with 2.2 equiv of sodium triphenylene gave **2** (53% yield by NMR) with concomitant formation of a trace amount of **3** (eq 2).[26] Increase

$$\underset{\mathbf{4}}{\mathrm{Ru(acac)_2}(\eta^4\text{-1,5-COD})} + 2\mathrm{Na/triphenylene} \xrightarrow[\mathrm{THF}]{-2\mathrm{Na(acac)},\ -\mathrm{triphenylene}} \mathbf{2} + \mathbf{3} \quad (2)$$

of sodium triphenylene to 3.2 equiv/equiv of **4** slightly increased the yield of **2** to 64% with concomitant formation of 6% of **3**, and a decrease to 1.1 equiv gave a 15% yield of **2** without formation of **3**. Thus, this methodology was found to give **2** as the dominant product, regardless of the quantity of sodium triphenylene.

Hydrogenolysis of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (5) in the Presence of Triphenylene. The third potential preparation method of (arene)ruthenium(0) complexes is hydrogenolysis of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**5**) in the presence of aromatic compounds.[27] Hydrogenolysis of **5** in the presence of 0.2 equiv of triphenylene followed by workup and recrystallization from THF gave the triruthenium complex [Ru(η^4-1,5-COD)]$_3$(μ^3-η^6:η^6:η^6-triphenylene) (**6**) in 16% yield based on triphenylene as orange crystals (eq 3). NMR study revealed that an independent



(3)

reaction of **5** with 0.2 equiv of triphenylene gave **6** (14%) and **2** (4%), but signals assignable to **3** were not detected under these conditions. When 0.3 equiv of triphenylene was employed for this reaction under similar conditions, the yield of **6** decreased, giving a mixture of **6** (5%), **2** (6%), and **3** (20%). Use of 1 equiv of triphenylene/equiv of **5** no longer gave **6**, but a mixture of **2** (54%) and **3** (4%) was obtained. Thus, hydrogenolysis of **5** in high Ru(η^4-1,5-COD)/triphenylene ratio was revealed to promote the formation of **6**.

Complex **6** was characterized by NMR spectra and elemental analysis. The ^{1}H NMR spectrum of **6** shows that all aromatic protons appear at relatively high magnetic field, where five signals resonate at δ 5.24 (4H), 5.53 (2H), 5.58 (2H), 5.80 (2H), and 5.88 (2H). This is consistent with the coordination of all aromatic rings to the Ru moieties. Since the presence of five sets of aromatic resonances in **6** clearly rules out a structure with C_3 symmetry, we can conclude that one of the three Ru(η^4-1,5-COD) fragments binds to the anti face. Consistently, ^{1}H$-^1$H COSY revealed that the olefinic protons in two equivalent COD ligands appeared as multiplets at δ 3.23 (4H) and 3.42 (4H), and those in one unique COD ligand resonated as a singlet at δ 3.08 (4H). These signals feature stereochemistry of the two equivalent and one inequivalent Ru(η^4-1,5-COD) fragments in C_2 and C_s sites, respectively, with rapid rotation along the (triphenylene)$-$Ru(η^4-1,5-COD) axis on the NMR time scale. According to the ^{1}H NMR spectrum, **6** showed nine singlets due to the coordinated arene carbons and six singlets due to the 1,5-COD carbons in the ^{13}C{^{1}H} NMR spectrum. This pattern also shows that one of the three Ru(η^4-1,5-COD) fragments is located on the anti face of the triphenylene ligand. Therefore, the stereochemistry of **6** was unequivocally determined as shown in eq 3.

Relations among Mono-, Di-, and Trinuclear Complexes. To shed light on the formation mechanisms for **3** and **6**, the following experiments were carried out. Treatment of the mononuclear complex **2** with 2 equiv of **1** in the presence of MeCN produced the dinuclear complex **3** in quantitative yield. It is worth noting that no formation of the trinuclear complex **6** was observed at all in this reaction. On the other hand, treatment of the dinuclear complex **3** with 1.3 equiv of triphenylene in MeCN gave 2 equiv of the mononuclear complex **2**. This result clearly shows that the Ru(η^4-1,5-COD) fragment transfers from **3** to triphenylene reversibly and that the following equilibrium between **2** and **3** favors the **2** side in the presence of free triphenylene (Scheme 1).

Scheme 1

$$\mathbf{2} \underset{+\text{triphenylene}}{\overset{+\text{“Ru}(\eta^4\text{-1,5-COD)”}}{\rightleftharpoons}} \mathbf{3} \underset{+\text{triphenylene}}{\overset{+\text{“Ru}(\eta^4\text{-1,5-COD)”}}{\rightleftharpoons}} \mathbf{6}$$

Although the reaction of the dinuclear complex **3** with **1** in MeCN did not produce the trinuclear complex **6** at all, the treatment of the dinuclear complex **3** with 5 equiv of **5** under hydrogen produced the trinuclear complex **6** in 11% yield with a trace amount of **2** and **3**. On the other hand, the treatment of **6** with 1 equiv of triphenylene in MeCN followed by workup gave a black solid containing four components, including **2** (48% based on **6**), **3** (24%), **6** (34%), and free triphenylene (112%). These experiments clearly indicate that these mono-, di-, and trinuclear ruthenium complexes are basically interconvertible by the transfer reaction of a Ru(η^4-1,5-COD) fragment, though the yields were poor.

Protonation of Triphenylene Complexes. An interesting property of the Ru(η^4-1,5-COD)(η^6-arene) complexes is their reversible protonation to give cationic hydrido complexes that were formulated as [RuH(η^4-1,5-COD)(η^6-arene)]$^+$. Treatment of the mononuclear complex **2** with HPF_6 in ether quantitatively gave a white solid which was assigned on the basis of the NMR spectra as the cationic hydrido complex [RuH(η^4-1,5-COD)-(η^6-triphenylene)][PF_6] ([**7**][PF_6]). The hydride in **7** resonated at δ -5.67 as a singlet. Addition of NEt_3 to a CH_2Cl_2 solution of [**7**][PF_6] regenerated the zerovalent complex **2** in 96% yield.

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In contrast to the mononuclear complex, protonation of the dinuclear complex **3** by HPF_6 gave a complex mixture involving [**7**][PF_6] (26% yield). Protonation of **6** irreversibly gave unidentified complexes.

Concluding Remarks

In summary, we have shown that the triphenylene ligand acts as 6π, 12π, and 18π donors toward Ru(0) fragments by (a) displacement of the naphthalene ligand in **1** by triphenylene, (b) 2e reduction of **4** by sodium triphenylene, and (c) hydrogenolysis of **5** in the presence of triphenylene. The sufficient aromaticity in the uncoordinated part of the aromatic molecule is evident from formation of these multinuclear complexes. As expected, the triphenylene/Ru ratio is a key factor in the formation of these multinuclear complexes for methods a and c but method b is independent of the ratio, probably due to the stoichiometry for the 2e reduction reaction of ruthenium(II) species. This study also revealed reversible interconversion among mono-, di-, and trinuclear ruthenium(0) complexes by transfer of a Ru(η^4-1,5-COD) fragment. These findings offer a route to new two-dimensional multimetallic clusters having Ru(η^4-1,5-COD) fragments on a π-conjugated plane.

Experimental Section

All manipulations and reactions were performed under dry nitrogen with use of standard Schlenk and vacuum-line techniques. Teterahydrofuran and hexane were distilled over sodium benzophenone ketyl, CH_2Cl_2 and acetonitrile were distilled from Drierite, and ethanol was dried over calcium chloride and distilled under nitrogen over magnesium ethoxide; these solvents were stored under nitrogen. The complexes Ru(η^4-1,5-COD)(η^6-naphthalene) (**1**),[2j] Ru(acac)$_2$(η^4-1,5-COD) (**4**),[28] and Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**5**)[29] were prepared according to literature procedures; in the case of **5**, magnetic stirring was used instead of sonication. All other reagents were obtained from commercial supplier (Wako Pure Chemical Ind.) and used as received. Chromatographic separation was carried out on Al_2O_3 (Merck, Activity I, 250 mesh). The NMR spectra were recorded on a JEOL LA300 (^{1}H at 300.4 MHz) or JEOL AL400 spectrometer (^{13}C at 100.2 MHz). The internal reference was either tetramethylsilane or the residual solvent peak ($CHCl_3$, $CHDCl_2$). $CDCl_3$ and CD_2Cl_2 were distilled over P_4O_{10} and stored under vacuum. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHN analyzer.

Ru(η^4-1,5-COD)(η^6-triphenylene) (2). Method A. To a THF solution (6 mL) of Ru(acac)$_2$(η^4-1,5-COD) (**4**; 454 mg, 1.12 mmol) was added a THF solution (10 mL) of sodium triphenylene (535 mg, 2.34 mmol) at −78 °C. The mixture was warmed to room temperature and stirred for 3 days at room temperature. The reaction mixture was filtrated through an alumina pad, and the resulting solution was evaporated under reduced pressure. NMR analysis of the residue showed formation of **2** in 53% yield with a trace amount of **3**. The yellow residue was washed with absolute ethanol (10 mL × 5) and then recrystallized from cold CH_2Cl_2/ethanol (−80 °C) to give a yellow powder of **2** in 6% yield (28.7 mg, 0.0657 mmol). Complex **2** was characterized spectroscopically. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.62 (m, 8H, COD), 3.0 (br s, 4H, COD), 5.53 (AA′BB′, 2H, coord aromatic protons), 6.12 (AA′BB′, 2H, coord aromatic protons), 7.6 (m, 4H, uncoord aromatic protons), 8.09 (dd, J = 7.8, 1.8 Hz, 2H, uncoord aromatic protons), 8.61 (dd, J = 7.8, 1.8 Hz, 2H, uncoord aromatic protons).

Method B. Ru(η^4-1,5-COD)(η^6-naphthalene) (**1**; 195 mg, 0.577 mmol) was treated with triphenylene (105.9 mg, 0.464 mmol) in MeCN at room temperature for 1 day. After evaporation of all volatile material under reduced pressure, a yellow-green solid was obtained (206.3 mg). The ^{1}H NMR spectrum of the product with use of 1,4-dioxane as an internal standard showed formation of complex **2** in 98% yield based on triphenylene with a trace amount of **3**.

[Ru(η^4-1,5-COD)]$_2$(μ_2-η^6:η^6-triphenylene) (3). An MeCN solution (10 mL) of a mixture of an excess amount of Ru(η^4-1,5-COD)(η^6-naphthalene) (**1**; 173 mg, 0.514 mmol) and triphenylene (38 mg, 0.17 mmol) was stirred at room temperature for 24 h. The resulting orange precipitate was separated by filtration, washed with MeCN (3 mL × 3 times), and dried under vacuum. The powder was recrystallized from cold dichloromethane (−80 °C) to give **3** as orange crystals in 21% yield based on triphenylene (22.8 mg, 0.81 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.7 (m, 16H, COD), 3.02 (m, 4H, COD), 3.13 (m, 4H, COD), 5.23 (d, J = 5.7 Hz, 2H, coord aromatic protons), 5.64 (d, J = 5.7 Hz, 2H, coord aromatic protons), 6.06 (t, J = 5.7 Hz, 2H, coord aromatic protons), 6.12 (t, J = 5.7 Hz, 2H, coord aromatic protons), 7.60 (AA′BB′, 2H, uncoord aromatic protons), 8.09 (AA′BB′, 2H, uncoord aromatic protons). Anal. Calcd for $C_{34}H_{36}Ru_2$: C, 63.14; H, 5.61. Found: C, 62.79; H, 5.80.

[Ru(η^4-1,5-COD)]$_3$(μ_3-η^6:η^6:η^6-triphenylene) (6). A THF solution (10 mL) of an excess amount of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**5**; 695 mg, 2.20 mmol) and triphenylene (104 mg, 0.456 mmol) was stirred under a hydrogen atmosphere (0.1 MPa) at room temperature for 40 h. The resulting black powder was separated by filtration, washed with hexane (10 mL × 6), and then extracted with dichloromethane (5 mL × 3) to give an orange solution. The solution was concentrated and kept at −80 °C to give **6** as orange crystals in 16% yield based on triphenylene (62.4 mg, 0.0730 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.9 (br m, 24H, COD), 3.08 (br s, 4H, COD), 3.23 (br s, 4H, COD), 3.42 (br s, 4H, COD), 5.24 (br s, 4H, coord aromatic protons), 5.53 (br s, 2H, coord aromatic protons), 5.58 (br s, 2H, coord aromatic protons), 5.80 (br s, 2H, coord aromatic protons). 5.88 (br s, 2H, coord aromatic protons). ^{13}C{^{1}H} NMR (100.2 MHz, CD_2Cl_2): δ 32.4 (s), 33.6 (s), 35.6 (s), 65.0 (s), 65.6 (s), 66.4 (s), 75.0 (s), 75.7 (s), 76.8 (s), 86.2 (s), 88.8 (s), 89.3 (s), 93.1 (s), 95.3 (s), 102.2 (s). Anal. Calcd for $C_{43}H_{48}Ru_3$: C, 58.93; H, 5.65. Found: C, 59.51; H, 5.52.

Reaction of Ru(η^4-1,5-COD)(η^6-triphenylene) (2) with Ru(η^4-1,5-COD)(η^6-naphthalene) (1). Complexes **2** (27.6 mg, 0.0631 mmol) and **1** (41.8 mg, 0.123 mmol) were placed in a Schlenk tube, into which MeCN (1 mL) was introduced by syringe. The resulting brown suspension changed to an orange solution by 10 min at room temperature. After 1 h, all volatile materials were removed under reduced pressure to give an orange powder (58.3 mg). The ^{1}H NMR analysis by use of 1,4-dioxane as an internal standard showed exclusive formation of complex **3**, and the product yield was estimated as 109%.

Reaction of [Ru(η^4-1,5-COD)]$_2$(μ_2-η^6:η^6-triphenylene) (3) with Triphenylene. Complex **3** (23.8 mg, 0.0360 mmol) and triphenylene (11.3 mg, 0.0496 mmol) were placed in a Schlenk tube, into which MeCN (1.0 mL) was introduced by hypodermic syringe. After the mixture was stirred for 1 day at room temperature, all volatile material was removed under vacuum to give a yellow powder. The NMR analysis of the powder showed formation of **2** in 204% yield with a trace amount of **3**.

Reaction of [Ru(η^4-1,5-COD)]$_3$(μ_3-η^6:η^6:η^6-triphenylene) (6) with Triphenylene. Complex **6** (17.3 mg, 0.0202 mmol) and triphenylene (4.6 mg, 0.0202 mmol) were placed in a Schlenk tube, into which MeCN (1 mL) was added by hypodermic syringe. After reaction for 1 day at room temperature, all volatile material was removed under vacuum to give a black solid. The ^{1}H NMR analysis

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of the black solid shows formation of **2** (48% based on **6**), **3** (24%), and **6** (34%) with free triphenylene (112%).

Reaction of [Ru(η^4-1,5-COD)]$_2$(μ_2-η^6:η^6-triphenylene)] (3) with Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (5) under Hydrogen. Complexes **3** (77.8 mg, 0.120 mmol) and **5** (188 mg, 0.598 mmol) were placed in a Schlenk tube, into which THF (4 mL) was introduced by syringe. After evacuation of N_2 gas, H_2 (0.1 MPa) was introduced into the Schlenk tube and the reaction system was stirred at room temperature for 24 h. After the reaction, all volatile material was removed under reduced pressure. The ^{1}H NMR analysis of the resulting solid showed formation of **6** in 11% yield with a trace amount of **2** and **3**.

Protonation of 2. Five drops of HPF_6 in Et_2O (excess) were added to a suspension of **2** (82.7 mg, 0.189 mmol) in Et_2O, and the mixture was stirred for 4 h at room temperature. The resulting white deposit was separated from the supernatant, followed by washing with Et_2O and hexane, and dried under vacuum. Recrystallization of the crude product from CH_2Cl_2/Et_2O gave a pale yellow powder of [RuH(η^4-1,5-COD)(η^6-triphenylene)][PF_6] ([**7**][PF_6]; 111.3 mg, 100%). ^{1}H NMR (CD_2Cl_2): δ −5.67 (s, 1H, Ru*H*), 1.0 (m, 2H, CH_2 in COD), 1.4 (br d, 2H, CH_2 in COD), 1.7 (br d, 2H, CH_2 in COD), 2.3 (m, 2H, CH_2 in COD), 3.6 (br m, 2H, C*H* in COD), 3.9 (br m, 2H, C*H* in COD), 6.60 (m, 2H, coord aromatic C*H*), 6.96 (m, 2H, coord aromatic C*H*), 7.9 (t, J = 8 Hz, 2H, uncoord aromatic C*H*), 8.0 (t, J = 8 Hz, 2H, uncoord aromatic C*H*), 8.41 (d, J = 8 Hz, 2H, uncoord aromatic C*H*), 8.86 (d, J = 8 Hz, 2H, uncoord aromatic C*H*).

Deprotonation of [7][PF$_6$]. The complex [**7**][PF_6] (7.7 mg, 0.013 mmol) in CD_2Cl_2 was treated with excess NEt_3 (10 μL). The NMR spectrum showed complete disappearance of [**7**][PF_6] and exclusive regeneration of **2** (96%).

X-ray Structure Determination of Ru(η^4-1,5-COD)(η^6-triphenylene) (2). Crystals of **2** were obtained from the dichloromethane solution. A summary of crystallographic data for **2** is given in Table 2. Data collection was carried out on a Rigaku AFC-7R diffractometer using graphite-monochromated Mo Kα radiation at −73 °C. A selected yellow crystal was mounted on a glass fiber with Paratone N oil. Cell parameters were obtained from 21 reflections with 2θ angles in the range 28.94 < 2θ < 29.95°. A total of 2395 reflections with $I > 5.0\sigma(I)$ was used in the refinement. The structure was solved by direct methods (SIR88)[30] in the *teXsan* package program[31] and refined by full-matrix least-squares cycles.

Table 2. Crystallographic Parameters for 2

empirical formula	$C_{26}H_{24}Ru$
formula wt	439.56
cryst color, habit	yellow, prismatic
crystal dimens (mm)	0.45 × 0.25 × 0.15
crystal syst	monoclinic
lattice type	primitive
lattice params	
a (Å)	8.594(9)
b (Å)	13.63(2)
c (Å)	8.87(1)
β (deg)	114.75(9)
V (Å^3)	943(2)
space group	$P2_1/m$ (No. 11)
Z	2
D_{calcd} (g cm^{-3})	1.548
F_{000}	448.00
μ(Mo Kα) (cm^{-1})	13.64
diffractometer	Rigaku AFC7R
radiation	Mo Kα (λ = 0.710 69 Å)
temp (°C)	−73.0
scan type	ω−2θ
scan rate (deg/min)	8.0
$2\theta_{max}$ (deg)	55.0
no. of rflns measd	
total	2395
unique	2340 (R_{int} = 0.054)
structure soln	direct methods (SIR88)
p factor	0.1810
no. of observns with $I > 5.00\sigma(I)$	1668
no. of variables	90
rfln/param ratio	18.53
residuals	
R	0.077
R_w	0.129
goodness of fit	1.34

Absorption corrections were applied by the ϕ-scan method. Ru(1) and C(4)−C(9) were refined with anisotropic temperature factors. Hydrogen atoms were placed in calculated positions, but they were not refined. Full-matrix least-squares refinement led to convergence with R = 0.077 and R_w = 0.129.

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Supporting Information Available: Full description of crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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