ORGANOMETALLICS

Synthesis and Property of Diruthenium Complexes Containing Bridging Cyclic Diene Ligands and the Reaction of Diruthenium Tetrahydrido Complex with Benzene Forming a μ - η^2 : η^2 -Cyclohexadiene Complex via Partial Hydrogenation on a Ru₂ Center

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Supporting Information

ABSTRACT: The syntheses, structures, and reactivities of diruthenium complexes having a five-, six-, and seven-membered cyclic diene ligands are discussed in this paper. While the μ - η^2 : η^2 -cyclohexadiene complex 3 was readily prepared by the reaction of the diruthenium tetrahydrido complex 1 with 1,3-cyclohexadiene, 3 was alternatively synthesized by the reaction of 1 with benzene via partial hydrogenation of benzene on a diruthenium plane. While the μ - η^2 : η^2 -cyclohexadiene ligand was liberated as benzene upon mild heating, the treatment of 3 with ^tBuNC and CO caused further migration of hydrido ligand to the C₆ moiety to yield the μ - η^2 -cyclohexenyl complex 6 and the μ -cyclohexylidene and cycloheptatriene also afforded the bridging cyclic diene complexes 10 and 11.



While the thermolysis of the μ - η^2 : η^2 -cyclopentadiene complex 10 resulted in the degradation of the cluster skeleton forming Cp*RuCp (12), the μ - η^2 : η^2 -cycloheptadiene complex 11 was stable upon heating. These differences can be attributed to the aromatization of the cyclic diene moiety.

INTRODUCTION

The properties of aromatic molecules coordinated to a multimetallic center have attracted considerable attention in relation to catalytic reactions performed on a metal surface.¹ Many bimetallic² and trimetallic complexes^{2d,3} having arene ligands have been synthesized thus far, and studies on these complexes provide important information about the structures and reactivities of adsorbed aromatic molecules in addition to the recent developments in surface chemistry; these studies afford highresolution images of aromatic molecules adsorbed on a metal surface.⁴

Previously, we reported a reaction of a diruthenium tetrahydrido complex, Cp*Ru(μ -H)₄RuCp* (Cp* = η^5 -C₅Me₅) (1), with triphenylphosphine to yield a diruthenium μ -phosphido complex, (Cp*Ru)₂(μ -PPh₂)(μ -H)(μ - η^2 : η^2 -C₆H₆) (2), as a result of a P–C bond cleavage (Scheme 1).⁵ Complex 2 has a bridging benzene ligand, which adopts a μ - η^2 : η^2 -coordination mode. The bridging benzene ligand of 2 is readily substituted by other aromatic molecules such as toluene, which is used as a solvent. Similarly, 2 reacts with 2,2'-bipyridine to form a μ - η^2 : η^2 bipyridine complex.⁶ This μ -bipyridine complex would be present in the catalytic cycle of the dehydrogenative coupling of pyridines. A facile exchange of the μ - η^2 : η^2 -arene probably occurs because of the recovery of aromaticity of the coordinated Scheme 1. Formation and Reactivity of μ -Phosphido: μ - η^2 : η^2 -benzene Complex 2



arene molecule, and this arene exchange is a crucial step of the catalytic cycle.

While the reaction of the triruthenium pentahydrido complex $\{Cp^*Ru(\mu-H)\}_3(\mu_3-H)_2$ with benzene and pyridine affords a face-capping arene complex,^{3d,7} reactivities of 1 with benzene

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have not been studied in detail thus far. Since 1 catalyzes the dehydrogenative coupling of 4-substituted pyridines,⁶ complex 1 is expected to be able to activate aromatic molecules as the triruthenium complex does. In this article, we report the reaction of 1 with benzene. The treatment of 1 with benzene resulted in the formation of a μ - η^2 : η^2 -cyclohexadiene complex, {Cp*Ru(μ -H)}₂(μ - η^2 : η^2 -C₆H₈) (3), instead of a μ -benzene complex due to the partial hydrogenation of benzene on a bimetallic center. Complex 3 is alternatively synthesized by the reaction of 1 with cyclohexadiene. This method is applied to the synthesis of other cyclic diene complexes, and the properties of the μ - η^2 : η^2 -diene complexes having a five-, six-, or seven-membered ring are also mentioned in this article.

RESULTS AND DISCUSSION



While a μ -arene ligand was formed on the bimetallic center of 2, μ -cyclohexadiene complex 3 was formed upon treatment of 1 with benzene at 70 °C (eq 1). Complex 3 was formed via partial hydrogenation of an aromatic ring on the bimetallic center of 1. Such a facile hydrogenation of benzene was unexpected. This is probably due to the electron-rich nature of the metal centers composed of $[Cp^*Ru]$ units. Upon coordination, the C₆ moiety would effectively stabilize the bimetallic system as diene rather than benzene due to a strong back-donation. However, this stabilization is in competition with the recovery of aromatization. When 3 was heated in tetrahydrofuran (THF), complex 1 was completely regenerated with the elimination of benzene. This implies that complex 3 was equilibrated with 1 via the elimination of benzene. This equilibrium was also confirmed by the H/D exchange of the C_6 fragment upon mild thermolysis of 3 in C_6D_6 . Upon heating at 70 °C, the benzene solution of 1 equilibrated with 3 in 72 h. At that point, the ratio of 1 to 3 was estimated at ca. 1:17. Because of the thermal instability of 1, the formation of a small number of polymetallic hydrido clusters, $\{Cp^*Ru(\mu-H)\}_3$ - $(\mu_3-H)_2 (7\%)^8$ and $(Cp^*Ru)_4(H)_6 (10\%)^9$ was also observed during the reaction. Complex 3 was isolated in 61% yield from the mixture by using column chromatography. Complex 3 was fully characterized by the ¹H and ¹³C NMR spectroscopy.



Complex 3 is alternatively synthesized by the reaction of 1 with a slightly excess amount of 1,3-cyclohexadiene at an ambient temperature with the elimination of dihydrogen. In this case, the reaction proceeded quantitatively, and 3 was isolated in 82% yield (eq 2). The reaction of 1 with 1,4-cyclohexadiene also afforded the μ -1,3-cyclohexadiene complex 3 via the isomerization of 1,4-cyclohexadiene (*vide infra*).

The formation of a 1,3-cyclohexadiene ligand, which adopts a μ - η^2 : η^2 -coordination mode, was confirmed by an X-ray diffraction study. Because there were two independent molecules having



Figure 1. Molecular structure of **3** with thermal ellipsoids at the 30% level of probability.

similar structural properties in the unit cell, only one molecule is shown in Figure 1. Selected bond distances and angles are listed in Table 1. Multimetallic complexes containing a μ - η^2 : η^2 -cyclohexadiene ligand have been known to exist; however, their examples are still limited.¹⁰

The two Cp* groups are attached to the metal centers in a cis geometry with respect to the Ru–Ru vector similar to a precedent μ - η^2 : η^2 -cyclohexadiene complex having indenyl groups.^{10a} Complex 3 adopts a coordinatively unsaturated 32-electron configuration; thus, a Ru=Ru double bond is anticipated according to the EAN rule. The value of the distance between the two ruthenium atoms (2.7391(15) Å) is in the upper limit of the reported values for a Ru=Ru bond (2.257–2.767 Å).¹¹ The elongation of the Ru=Ru distance is ascribed to the ring size of the bridging diene moiety. As will be mentioned later, the Ru=Ru distance is increased to 2.7833(4) Å upon the bridging coordination of a sevenmembered ring in 11, while that of μ -cyclopentadiene complex 10 is reduced to 2.692(6) Å.

Upon the $\eta^2:\eta^2$ -coordination of the cyclohexadiene ligand, the six-membered ring is folded around the C(1)-C(4) vector and the dihedral angle between the C(1)-C(2)-C(3)-C(4) and C(1)-C(4)-C(5)-C(6) planes is estimated at ca. 10°. The length of the coordinated C=C bond is on average 1.44 Å, which is less than the inner C(2)-C(3) distance by ca. 0.03 Å. These results suggest a localization of the π -electrons at C(1)-C(2) and C(3)-C(4) bonds as seen in the precedent μ - $\eta^2:\eta^2$ -diene complexes.^{10,12}

In the ¹H NMR spectrum of 3, a signal derived from the Cp^{*} groups was observed at δ 1.77 ppm. This shows that complex 3 has a time-averaged structure containing a pseudo mirror plane bisecting the Ru=Ru bond as well as the μ -cyclohexadiene ligand. Two sharp signals assignable with the hydrido ligands were observed at δ –9.00 (H^a) and –22.88 (H^b) ppm with 4.8 Hz spin-spin coupling between each other. The shapes of these signals did not change and were still sharp up to 80 °C, which indicates that the site exchange between the hydrido ligands within the NMR time scale was unimportant.

Four signals for the cyclohexadiene moiety were observed in the ¹H NMR spectrum, as shown in Chart 1. Among them, the protons derived from the diene moiety resonated at δ 4.98 and 3.43 ppm. These resonances considerably shifted toward a higher magnetic field than those of the free 1,3-cyclohexadiene, and the chemical shifts are comparable to those of the precedent μ -1, 3-cyclohexadine complexes.¹⁰ Signals for the methylene moieties

Table 1. Selected B	ond Distances (Å) an	nd Angles (deg) for 3			
Ru(1)-Ru(2)	2.7391(15)	Ru(1) - C(1)	2.194(15)	Ru(1) - C(2)	2.241(15)
Ru(2) - C(3)	2.257(16)	Ru(2) - C(4)	2.202(14)	C(1) - C(2)	1.48(2)
C(1) - C(6)	1.534(19)	C(2) - C(3)	1.463(18)	C(3) - C(4)	1.421(19)
C(4) - C(5)	1.560(19)	C(5) - C(6)	1.550(19)		
Ru(3)-Ru(4)	2.7406(17)	Ru(3)-C(27)	2.217(13)	Ru(3) - C(28)	2.245(16)
Ru(4) - C(29)	2.221(15)	Ru(4) - C(30)	2.234(15)	C(27) - C(28)	1.42(2)
C(27) - C(32)	1.54(2)	C(28)-C(29)	1.47(2)	C(29) - C(30)	1.42(2)
C(30) - C(31)	1.53(2)	C(31) - C(32)	1.57(2)		
C(1)-Ru(1)-C(2)		38.9(5)	C(3)-Ru(2)-C(4)		37.2(5)
C(2) - C(1) - C(6)		122.2(12)	C(1)-C(2)-C(3)		119.1(14)
C(2) - C(3) - C(4)		120.5(14)	C(3) - C(4) - C(5)		123.6(12)
C(4) - C(5) - C(6)		115.4(11)	C(1) - C(6) - C(5)		116.4(12)
C(27)-Ru(3)-C(28)		37.2(5)	C(29)-Ru(4)-C(30)		37.2(5)
C(28)-C(27)-C(32)		124.5(14)	C(27)-C(28)-C(29)		119.2(14)
C(28) - C(29) - C(30)		120.2(15)	C(29) - C(30) - C(31)		123.4(14)
C(30) - C(31) - C(32)		117.1(13)	C(27) - C(32) - C(31)		113.5(13)

Chart 1. Selected ¹H NMR Data of 3



appeared at δ 2.14 and 1.22 ppm, which are assignable to the *exo*and *endo*-H, respectively.

Because of the magnetic inequivalence, the ¹H signals of the bridging cyclohexadiene moiety showed complicated coupling patterns. By the computer simulation, we evaluated the coupling constants among these protons (complete details of the simulation are summarized in the Supporting Information). The value of the geminal coupling constant between the *exo*-H (δ 2.14) and the endo-H (δ 1.22) was evaluated at -14.6 Hz. As will be mentioned later, a spin-saturation-transfer phenomenon was observed only between the methylene signal at δ 1.22 and the hydrido signal at δ –22.88. This enables us to assign the signal at δ 1.22 to endo-H, and the position of H^b is found to be below the methylene carbons. As seen in Figure 2a, the signal for the exo-H exhibited a more complicated coupling pattern than that for the *endo*-H because of the long-range coupling with H^b $({}^{4}J = 1.35 \text{ Hz})$. A similar long-range coupling with a hydrido ligand was also observed for the μ_3 -dimetalloallyl complex: a methine proton at the 2-position of the dimetalloallyl group exhibited ⁴*J* coupling with a hydrido ligand (0.5-3.5 Hz).¹³ A similar but considerably large long-range coupling between the *endo*-H and the hydride was observed in μ - η^2 : η^2 -cyclopentadiene



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Figure 2. ¹H NMR spectra of **3** measured at 80 °C showing the methylene region: (a) without irradiation, (b) irradiation at δ -22.92 ppm.

Scheme 2. Plausible Mechanism of the Site-Exchange between *endo*-H and H^b in 3



complex **10** and its iron analogue,¹⁴ in which the magnitude of ${}^{4}J_{H-H}$ was estimated to be 7.8 and 6.3 Hz, respectively.

Although the site exchange between the hydrido ligands was negligible within the NMR time scale, another fluxional process arising from the motion of H^b was observed. Upon irradiation of H^b at 80 °C, the intensity of the *endo*-H signal decreased by ca. 80%, while those of the *exo*-H and H^a remained unchanged.

Scheme 3. Plausible Mechanism for the Formation of μ - η^2 : η^2 -Cyclohexadiene Complex 3



(Figure 2b). This clearly proves that the site exchange occurred only between H^b and the *endo*-H.

This site exchange can be rationalized by the formation of a μ - $\eta^3:\eta^2$ -cyclohexadienyl intermediate 4; this formation involves oxidative addition of one of the *endo*-C-H bonds (Scheme 2). Whereas complex 3 adopted a coordinatively unsaturated 32-electron configuration, intermediate 4 formally adopted a coordinatively saturated 34-electron configuration. A related bimetallic complex, which possesses a μ - $\eta^3:\eta^2$ -cyclohexadienyl ligand, was known and structurally characterized.¹⁵

A partially deuterated μ -cyclohexadiene complex, $3 \cdot d_2$, was prepared by the reaction of $1 \cdot d_4^{16}$ with 1,3-cyclohexadiene. The ¹H NMR spectrum of $3 \cdot d_2$ showed the incorporation of ¹H atoms into both the hydrido positions, H^a and H^b, with the same amount (0.25 H) and a decrease in the intensity of the *endo*-H signal by 25%. The incorporation of deuterium atoms into other positions, especially the *exo*-H position, was not observed. This result also strongly supports the formation of the μ - η^3 : η^2 cyclohexadienyl intermediate 4. The slower site exchange process between H^a and H^b would cause the incorporation of protons at the both hydrido positions.

The elimination of the μ - η^2 : η^2 -cyclohexadiene ligand in 3 as benzene is possibly due to the stabilization arising from aromatization. Further migration of the allylic proton of the μ cyclohexadienyl intermediate 4 onto the metal center led to the formation of a benzene ligand, which would readily eliminate from the metal center and regenerate the tetrahydrido complex 1. This process is the reverse of the formation of 3 by the reaction of 1 with benzene via the formation of the μ - η^3 : η^2 -cyclohexadienyl intermediate 4 (Scheme 3).

The intermediate **4** can also be formed by the reaction of **1** with 1,4-cyclohexadiene. A 1,4-diene coordination to a bimetallic center was found in a μ - η^2 : η^2 -1,4-benzoquinone complex, which was obtained by the reaction of **1** with benzoquinone.¹⁷ Therefore, it is reasonable to assume that 1,4-diene complex **5** is produced by the reaction of **1** with 1,4-cyclohexadiene at first. The subsequent migration of an allylic proton onto the metal

center would afford the μ -cyclohexadienyl complex 4, which would easily isomerize to the μ -1,3-cyclohexadiene complex 3.

The facile elimination of benzene from 3 suggests the possibility of catalytic dehydrogenation of cyclohexadiene using 1 as a catalyst. The reaction of 1 with 16 equiv amounts of 1, 3-cyclohexadiene was then examined; the reaction carried out at 70 °C for 8 h resulted in the formation of benzene in 26% yield (eq 3). The yields of cyclohexane and cyclohexane that were formed in the reaction were as low as 0.8% and less than 0.1%, respectively. These facts clearly indicate that cyclohexadiene did not act as a hydrogen acceptor. The formation of dihydrogen was confirmed by the GLC analysis of the gas phase.

If the μ -cyclohexadiene ligand in 3 was liberated as cyclohexadiene or cyclohexene, complex 1 could have catalyzed the partial hydrogenation of benzene upon treatment with dihydrogen. The liberation of 1,3-cyclohexadiene from a bimetallic center was observed for {CpV(μ -H)}₂(μ - η^4 : η^4 -C₆H₆) (Cp = C₅H₅) upon treatment with CO as a result of the migration of hydrido ligands onto the C₆ fragments.^{2b} However, the liberation of cyclohexadiene or cyclohexene from 3 was not observed during the hydrogenation of 3; the treatment of 3 with pressurized dihydrogen (10 atm) resulted in the quantitative regeneration of the tetrahydrido complex 1 with a concomitant formation of benzene caused probably by the equilibrium between 1 and 3 as shown in eq 1.

We, then, examined the reaction of **3** with *tert*-butylisocyanide. In this case, the elimination of the C₆ moiety was suppressed, and the μ - η^2 -cyclohexenyl complex **6** was obtained in 88% yield (eq 4). The formation of **6** was rationalized by the insertion of one of the C=C bonds into a Ru–H bond. During this reaction, the tetraisocyanido complex **7** was also formed as a consequence



Figure 3. Molecular structure of **6** with thermal ellipsoids at the 30% level of probability.

of the elimination of the cyclohexadiene ligand; however, the amount of 7 was considerably low.¹⁸



In the ¹H NMR spectrum of **6**, the two signals derived from the Cp* groups resonated at δ 1.84 and 2.05 ppm, respectively; this shows that the two ruthenium centers have inequivalent environments. The signal for the hydrido ligand was observed at δ –13.57 ppm with the intensity of 1 H. These results indicate that one of the two hydrido ligands in **3** migrates to the cyclohexadiene ligand to form a μ -cyclohexenyl ligand. The signal for the σ -bonded carbon of the cyclohexenyl moiety appeared in a significantly higher magnetic field and resonated at δ 4.3 ppm (d, $J_{C-H} = 138$ Hz). The formation of a μ -cyclohexenyl ligand was also unambiguously confirmed by an X-ray diffraction study using the orange single crystal obtained from the cold pentane solution.

The molecular structure of **6** is shown in Figure 3, and selected bond distances and angles are listed in Table 2. The C(2) and C(3) atoms are π -bonded to Ru(1), and the C(1) atom is σ -bonded to Ru(2). Each ruthenium atom adopts a three-legged piano stool structure with the hydrido, isocyanide, and cyclohexenyl group. The two *tert*-butylisocyanido ligands are coordinated in a trans geometry with respect to the Ru–Ru vector.

While the isocyanido group on Ru(1) is linear, that on Ru(2) adopts a bent structure; the angles C(7)-N(1)-C(8) and C(12)-N(2)-C(13) are estimated at $170.61(18)^{\circ}$ and $135.12(16)^{\circ}$, respectively. This indicates that the isocyanido group on Ru(2) underwent strong back-donation from the metal

center. Since the cyclohexenyl moiety is π -bonded to Ru(1), the back-donation to the isocyanido group on Ru(1) is considerably reduced. The difference in the magnitude of back-donation is also reflected in the bond distances around C–N and Ru–C bonds; the N(2)–C(12) bond is longer than N(1)–C(7) by 0.04 Å, and Ru(2)–C(12) is shorter than Ru(1)–C(7) by 0.05 Å. These data are consistent with the enhanced back-donation from Ru(2) to the $\pi^*(CN)$ orbital. These isocyanido groups are also distinguished from each other by IR spectroscopy. In the IR spectrum of **6**, two sharp adsorptions are seen at 2045 and 1838 cm⁻¹, which are assignable to $\nu(CN)$ of the linear and the bent isocyanido groups, respectively.



The reaction of **3** with the isoelectronic CO was also investigated. Because of its small size, three molecules of CO were incorporated into the bimetallic center, which caused further migration of the hydrido ligand onto the C₆ moiety. The treatment of **3** with 1 atm of CO resulted in the formation of a μ -cyclohexylidene complex, {Cp*Ru(CO)}₂(μ -C₆H₁₀)(μ -CO) (**8**), in 47% yield (eq 5). The formation of a considerable amount of {Cp*Ru(CO)}₂(**9**) was also observed. Complex **8** did not react with CO even under forced conditions. This shows that these complexes are formed independently, and the formation of **9** was rationalized by the reaction of the regenerated complex **1** with CO.

The molecular structure of **8** was confirmed by an X-ray diffraction study as shown in Figure 4, which clearly shows the formation of a μ -cyclohexylidene ligand. Two of the three CO ligands are coordinated as terminal ligands in a trans geometry with respect to the Ru–Ru vector, and the third CO molecule bridges the two ruthenium centers. The Ru(1)–Ru(2) distance (2.7569(6) Å) is typical for a Ru–Ru single bond, which makes each ruthenium center coordinatively saturated according to the EAN rule. The sum of the interior angles of the Ru₂C₂ core is 359.9°, and the Ru(1), Ru(2) C(1), and C(7) atoms are coplanar.

The formation of a μ -cyclohexylidene ligand was rationalized as shown in Scheme 4. Because CO closely resembles ^tBuNC, it is reasonable to consider the μ -cyclohexenyl intermediate **A**. The intermediate **A** equilibrates with isomeric vinyl intermediate **B**, which would be formed via the oxidative addition of an olefinic C-H bond and the consecutive reductive C-H bond formation. The insertion of the C=C bond into a Ru-H bond afforded a coordinatively unsaturated μ -cyclohexylidene intermediate, which captured the third CO molecule to form 7.

The relevant cyclic diene complexes were also synthesized by the reaction of 1 with cyclopentadiene and cycloheptatriene (eqs 6 and 7). In the reaction of 1 with cycloheptatriene, the μ -cycloheptadiene complex 11 was obtained as a consequence of hydrogenation. Complexes 10 and 11 were characterized by ¹H and ¹³C NMR spectra; their molecular structures were

Гat	ole 2.	Selected	Bond	Distances	(A)	and	Angle	es (d	eg)	for (5
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Ru(1)-Ru(2)	3.07636(18)	Ru(1) - C(2)	2.3125(16)	Ru(1) - C(3)	2.2107(16)
Ru(1) - C(7)	1.9050(17)	Ru(2) - C(1)	2.1799(16)	Ru(2) - C(12)	1.8473(17)
N(1) - C(7)	1.166(2)	N(1) - C(8)	1.448(2)	N(2)-C(12)	1.208(2)
N(2) - C(13)	1.472(2)	C(1) - C(2)	1.471(2)	C(1) - C(6)	1.529(2)
C(2) - C(3)	1.413(2)	C(3) - C(4)	1.516(2)	C(4) - C(5)	1.528(2)
C(5) - C(6)	1.523(2)	C(8) - C(9)	1.518(3)	C(8) - C(10)	1.505(3)
C(8) - C(11)	1.529(3)	C(13) - C(14)	1.511(3)	C(13) - C(15)	1.525(3)
C(13)-C(16)	1.522(3)				
C(2)-Ru(1)-C(3)		36.31(6)	Ru(1)-Ru(2)-C(1)	1	74.90(4)
C(7)-N(1)-C(8)		170.61(18)	C(12) - N(2) - C(13))	135.12(16)
C(2) - C(1) - C(6)		113.17(14)	C(1)-C(2)-C(3)		124.18(15)
C(2) - C(3) - C(4)		119.47(15)	C(3) - C(4) - C(5)		112.77(14)
C(4) - C(5) - C(6)		110.48(15)	C(1) - C(6) - C(5)		112.77(14)



Figure 4. Molecular structure of 8 with thermal ellipsoids at the 30% level of probability.

determined by the X-ray diffraction studies, which are shown in Figures 5 and 6, and selected bond distances and angles of the complexes are listed in Table 4.



The two Cp^{*} groups adopted a cis geometry with respect to the Ru–Ru vector as seen in 3. The Ru(1)–Ru(2) distance of 2.6922(4) Å in 10 corresponds to the Ru=Ru double bond, which is anticipated according to the EAN rule. The Ru–Ru distance of 2.692(6) Å was reported for the closely related

Table 3. Selected Bond Distances (Å) and Angles (deg) for 8

Ru(1)-Ru(2)	2.7569(6)	Ru(1)-C(2)	1) 2.138(4)	Ru(1) - C(7)	2.035(4)
Ru(1)-C(8)	1.830(4)	Ru(2)-C(2)	1) 2.121(3)	Ru(2) - C(7)	2.021(4)
Ru(2)-C(9)	1.843(4)	C(1) - C(2)) 1.517(5)	C(1) - C(6)	1.534(5)
C(2) - C(3)	1.537(5)	C(3) - C(4)) 1.511(6)	C(4) - C(5)	1.523(6)
C(5) - C(6)	1.535(5)	C(7) - O(1) 1.185(5)	C(8) - O(2)	1.160(5)
C(9) - O(3)	1.155(5)				
C(1)-Ru(1)-	C(7)	96.32(14)	Ru(2)-Ru(1	-C(8)	92.59(12)
C(1)-Ru(2)-	C(7)	97.29(15)	Ru(1)-Ru(2)	C(9) - C(9)	90.80(12)
Ru(1) - C(1) -	Ru(2)	80.67(12)	Ru(1) - C(7)	-Ru(2)	85.64(15)
Ru1-C(1)-C(1)	(2)	119.4(3)	Ru1-C(1)-	C(6)	118.1(3)
Ru2-C(1)-C(1)	(2)	115.4(2)	Ru2-C(1)-	C(6)	114.6(2)
C(2) - C(1) -	C(6)	107.0(3)	C(1) - C(2)	-C(3)	115.8(3)
C(2) - C(3) -	C(4)	112.0(3)	C(3) - C(4)	-C(5)	109.9(3)
C(4) - C(5) -	C(6)	110.6(3)	C(1) - C(6)	-C(5)	112.0(3)
Ru(1) - C(7) -	O(1)	137.8(3)	$\operatorname{Ru}(2) - \operatorname{C}(7)$	-O(1)	136.6(3)

diruthenium complex {CpRu(μ -CH₂)}₂(μ - η^2 : η^2 -C₅H₆).^{12b} The Ru–Ru distance of **10** is less than those of μ -cyclohexadiene complex **3** (2.7391(15) Å) and μ -cycloheptadiene complex **11** (2.7833(4) Å), because of the small ring-size of the coordinated cyclic diene ligand in **10**. On the other hand, the Ru–Ru distance is significantly greater than the Fe–Fe distance of the iron analogue, {Cp*Fe(μ -H)}₂(μ - η^2 : η^2 -C₅H₆) (2.483(1) Å), which clearly reflects the difference between the ionic radii of iron and ruthenium.¹⁴

The cyclopentadiene ligand in **10** bridges the two ruthenium centers in a μ - η^2 : η^2 -fashion. The methylene carbon of the cyclopentadiene ligand, C(1), is located above the plane composed of the four carbon atoms of the diene moiety by ca. 0.25 Å. The lengths of the coordinated C=C bond were 1.375(8) and 1.380(8) Å, which were less than that of the inner C-C single bond by ca. 0.10 Å. While the lengths of the C=C bond of the diene moiety were similar to those of the iron analogue, the length of the inner C-C single bond was significantly greater by 0.07 Å.¹⁴ This further shows the difference between the M-M bond length of Ru-Ru and Fe-Fe.

In the ¹H NMR spectrum of **10**, four signals assignable to the cyclopentadiene moiety were observed at δ 2.45 (*endo*-H), 3.75 (*exo*-H), 4.19, and 5.13 ppm (Chart 2). Similar to the ¹H NMR spectrum of **3**, these signals showed complicated coupling patterns arising from the magnetically inequivalent circumstance. By using simulation, the coupling constants of these protons were evaluated (see Supporting Information). A significantly large

Scheme 4. Plausible Mechanism of the Reaction of 3 with CO





Figure 5. Molecular structure of **10** with thermal ellipsoids at the 30% level of probability.



Figure 6. Molecular structure of **11** with thermal ellipsoids at the 30% level of probability.

spin–spin coupling of ${}^{4}J_{H-H}$ (7.75 Hz) was observed between the *exo*-H and H^b in the simulation. Unlike complex **3**, **10** does not show any fluxional behavior within the NMR time scale.



The thermolysis of **10** in C_6D_6 at 70 °C resulted in the fragmentation of the Ru_2 core, and a pentamethytlruthenocene, Cp*RuCp (**12**), was formed in 45% yield (eq 8). The driving force for this reaction could be the stabilization due to the

Table 4.	Selected	Bond	Distances	(Å)	and	Angles	(deg)	for
10 and 1	1							

10		11	
Ru(1)-Ru(2)	2.6922(4)	Ru(1)-Ru(2)	2.7834(4)
Ru(1) - C(2)	2.179(4)	Ru(1) - C(3)	2.209(4)
Ru(1) - C(3)	2.250(5)	Ru(1) - C(4)	2.248(4)
Ru(2) - C(4)	2.210(4)	Ru(2) - C(5)	2.189(4)
Ru(2) - C(5)	2.178(5)	Ru(2) - C(6)	2.199(5)
		C(1) - C(2)	1.512(7)
C(1) - C(2)	1.523(8)	C(2) - C(3)	1.492(7)
C(2) - C(3)	1.375(8)	C(3) - C(4)	1.384(6)
C(3) - C(4)	1.477(7)	C(4) - C(5)	1.452(6)
C(4) - C(5)	1.380(8)	C(5) - C(6)	1.402(6)
C(5) - C(1)	1.483(9)	C(6) - C(7)	1.504(7)
		C(7) - C(1)	1.512(8)
C(2)-Ru(1)-C(3)	36.1(2)	C(3)-Ru(1)-C(4)	36.18(16)
C(4) - Ru(2) - C(5)	36.6(2)	C(5)-Ru(2)-C(6)	37.27(16)
		C(2) - C(1) - C(7)	114.4(5)
C(2) - C(1) - C(5)	101.7(5)	C(1) - C(2) - C(3)	119.0(4)
C(1)-C(2)-C(3)	108.5(5)	C(2) - C(3) - C(4)	128.6(4)
C(2) - C(3) - C(4)	109.0(5)	C(3) - C(4) - C(5)	128.0(4)
C(3) - C(4) - C(5)	107.2(5)	C(4) - C(5) - C(6)	127.3(4)
C(4) - C(5) - C(1)	110.7(5)	C(5) - C(6) - C(7)	129.2(4)
		C(6) - C(7) - C(1)	120.7(4)

Chart 2. Selected ¹H NMR Data of 10



formation of the aromatic $C_5H_5^-$. The fate of the rest of the $[Cp^*Ru]$ fragment is unknown at present.¹⁹ The formation of **12**

Table 5. Crystallographic Data for 3, 6, 8, 10, and 11

	3	6	8	10	11				
(a) Crystal Data									
empirical formula	C26 H40Ru2	C36 H58N2Ru2	C29 H40 O3 Ru2	C25 H38 Ru2	C ₂₇ H ₄₂ Ru ₂				
fw	554.72	720.98	638.75	540.69	568.75				
cryst description	block	platelet	block	needle	needle				
cryst color	red	orange	yellow	orange	red				
cryst size (mm)	$0.08\times0.07\times0.05$	$0.16 \times 0.11 \times 0.04$	0.14 imes 0.08 imes 0.07	0.19 imes 0.08 imes 0.02	0.12 imes 0.08 imes 0.04				
crystallizing solution	pentane (-30 °C)	pentane (-30 °C)	THF (25 °C)	pentane (-30 °C)	pentane (25 °C)				
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic				
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P\overline{1}$ (#2)	$P2_1/n$ (#1014)	$P2_1/c$ (#14)				
lattice params	a = 14.9607(10) Å	a = 11.6809(3)	a = 9.7930(15) Å	a = 8.3926(4) Å	a = 8.0533(8) Å				
	b = 19.8883(12) Å	b = 8.8655(2)	b = 9.8397(18) Å	b = 26.2462(11) Å	b = 36.216(3)Å				
	c = 17.2271(12) Å	c = 33.7174(7)	c = 15.993(2) Å	c = 10.9157(4) Å	c = 9.1233(10) Å				
			$\alpha = 100.994(5)^{\circ}$						
	$\beta = 109.262(2)^{\circ}$	$\beta=98.3910(7)^\circ$	$\beta = 100.953(5)^\circ$	$\beta = 104.1550(14)^\circ$	$\beta = 109.657(3)^\circ$				
			$\gamma=112.116(5)^\circ$						
$V(\text{\AA}^3)$	4838.9(6)	3454.30(15)	1342.2(4)	2331.44(17)	2505.8(4)				
Z value	8	4	2	4	4				
$D_{\rm calc}$ (g/cm ³)	1.523	1.386	1.581	1.540	1.508				
measurement temp (°C)	-120	-150	-100	-100	-100				
μ (Mo K α) (mm ⁻¹)	1.257	0.900	1.153	1.302	1.216				
		(b) Intensity Measure	ements						
diffractometer	RAXIS-RAPID	RAXIS-RAPID	RAXIS-RAPID	RAXIS-RAPID	RAXIS-RAPID				
radiation	Mo K α								
monochromator	graphite	graphite	graphite	graphite	graphite				
$2 heta_{ m max}$	50°	55°	55°	55°	55°				
reflns collected	30 1 1 6	49 966	13 243	23 098	22 008				
indep reflns	8997 ($R_{\rm int} = 0.1938$)	7886 ($R_{\rm int} = 0.0374$)	6102 ($R_{\rm int} = 0.0422$)	5445 ($R_{\rm int} = 0.0571$)	5826 ($R_{\rm int} = 0.0722$)				
reflns obsd (>2 σ)	3569	7072	4915	4233	4045				
abs corr type	empirical	empirical	empirical	empirical	empirical				
abs transmn	0.2198 (min.),	0.8657 (min.),	0.7017 (min.),	0.7129 (min.),	0.5840 (min.),				
	1.0000 (max.)	0.9623 (max.)	1.0000 (max.)	1.0000 (max.)	1.0000 (max.)				
		(c) Refinement (Shelx	d-97-2)						
$R_1 (I > 2\sigma(I))$	0.0777	0.0204	0.0395	0.0384	0.0354				
$wR_2 (I > 2\sigma(I))$	0.1687	0.0472	0.0868	0.0925	0.0660				
R_1 (all data)	0.1974	0.0250	0.0535	0.0533	0.06489				
wR ₂ (all data)	0.2318	0.0489	0.0939	0.1012	0.0843				
data/restraints/params	8709/0/526	7886/0/581	6087/0/415	5301/0/272	5696/0/320				
GOF	0.927	1.056	1.027	1.042	1.081				
largest diff peak and hole (e $Å^{-3}$)	1.021 and -1.807	0.484 and -0.347	3.275 and -1.401	0.869 and -0.749	0.866 and -0.786				

was confirmed by comparing its ¹H NMR spectrum with the reported data.²⁰

Unlike the μ -cyclohexadiene ligand in 3, the μ -cycloheptadiene ligand in 11 was not substituted by benzene, and 11 was stable for at least 3 days in benzene at 70 °C. This stability possibly arose from the difficulty in the aromatization of the seven-membered ring.

The hydrocarbyl moieties were tightly bound to the multimetallic center of an electron-rich cluster composed of the [Cp*Ru] units. This stabilizes the cluster compound; thus, the bonds in such complexes are very strong and cannot release a hydrocarbyl moiety from a multimetallic center as seen in complex 11. Under forced conditions, a hydrocarbyl ligand was eliminated as an organic molecule; however, the reaction rate was very slow. The treatment of a trimetallic *closo*-ruthenacyclopentadiene complex, $(Cp^*Ru)_2\{Cp^*Ru(\mu_3-C_6H_4-C(H)=C-(C_3H_8)-)\}(\mu-H)$, with 7 atm of dihydrogen at 180 °C afforded a triruthenium pentahydrido complex, $\{Cp^*Ru(\mu-H)\}_3(\mu_3-H)_2$, with the elimination of *n*-pentylbenzene in a low yield of 10% in 3 days.²¹

CONCLUSIONS

We synthesized novel bimetallic complexes having cyclic diene ligands by the reactions of the diruthenium tetrahydrido complex 1 with several cyclic dienes. All the cyclic diene ligands adopted an s-cis coordination mode and bridged two metal nuclei in a μ - η^2 : η^2 -fashion. The μ -cyclohexadiene complex 3

was alternatively synthesized by the reaction of 1 with benzene via partial hydrogenation of benzene on the bimetallic center. The facile hydrogenation of aromatic molecules was possibly directed by the electron-rich metal center composed of the [Cp*Ru] units, and the formation of 3 can be attributed to the partial hydrogenation of benzene. However, the cyclohexadiene ligand formed in 3 was readily eliminated as benzene upon mild heating.

In contrast to the μ -cyclohexadiene ligand in 3, the μ -cycloheptadiene ligand in 11 was sufficiently robust against elimination. This distinct contrast was possibly due to the absence of the aromatization process for the hydrocarbyl ligand. This fact indicates the construction of novel catalytic systems on a multimetallic site. These results imply that the aromatization of the coordinated hydrocarbyl group can overcome the gravity of the multimetallic center.

Although cyclohexene or cyclohexadiene did not eliminate from the bimetallic center at present, the treatment of **3** with 2edonors suppresses the elimination of benzene and promotes further migration of hydrido onto the C_6 moiety. The introduction of an appropriate ligand can functionalize the C_6 moiety. Particularly, the μ -cyclohexenyl ligand in **6** can be assumed to be an allyl group. We continued the research of the reactivity of **3** with various substrates in order to introduce a functional group in the C_6 moiety and eliminate the C_6 moiety as cyclohexene.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive compounds were manipulated using standard Schlenk and high-vacuum line techniques under an argon atmosphere. Dehydrated benzene, toluene, pentane, and THF used in this study were purchased from Kanto Chemicals and stored under an argon atmosphere. Benzene- d_6 and THF-d₈ were distilled from sodium benzophenone ketyl and stored under an argon atmosphere. Cyclopentadiene was prepared by the cracking of dicyclopentadiene before use. Other materials were used as purchased. ¹H and ¹³C NMR spectra were recorded on a Varian INOVA-400 spectrometer. ¹H NMR spectra were referenced to tetramethylsilane as an internal standard. ¹³C NMR spectra were referenced to the natural-abundance carbon signal of the solvent employed. IR spectra were recorded on a Jasco FTIR4200 spectrophotometer. GLC analyses were performed on Shimadzu GC-17A and Shimadzu GC-14B with helium gas as a carrier. Elemental analysis was performed on a Perkin-Elmer 2400II series CHN analyzer. Complex 1 was prepared according to a previously published method.²²

X-ray Diffraction Studies. Single crystals of 3, 6, 8, 10, and 11 for an X-ray analysis were obtained directly from the preparations described below and mounted on nylon Cryoloops with Paratone-N (Hampton Research Corp.). Diffraction experiments were performed on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71069 Å). In all samples, cell refinement and data reduction were performed using the PROCESS-AUTO program.²³ Intensity data were corrected for Lorentz-polarization effects and for empirical absorption. The structures were solved by the direct method using the SHELX-97 program package.²⁴ The structures were refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculation on F^2 using the SHELX-97 program package except for the disordered Cp* group in 10. All hydrogen atoms were refined isotropically. Neutral atom scattering factors were obtained from the standard sources.²⁵ The metal-bound hydrogen atoms in 6, 10, and 11 were located in the difference Fourier map and refined isotropically, while the positions of the metal-bound hydrogen atoms of 3 were not determined. Crystal data and results of the analysis are listed in Table 5.

NMR Simulations. NMR simulations for 3 and 10 were performed using gNMR v4.1.0. (1995–1999 Ivory Soft). Final simulated line shapes were obtained via an iterative parameter search upon the coupling constants among the hydride ligands and the protons on the diene moiety. Complete details of the fitting procedure and results are shown in Supporting Information.

Preparation of μ - η^2 : η^2 -Cyclohexadiene Complex {Cp*Ru- $(\mu-H)_{2}(\mu-\eta^{2}:\eta^{2}-C_{6}H_{8})$ (3). Pentane (10 mL) and diruthenium tetrahydrido complex 1 (0.208 g, 0.44 mmol) were charged in a reaction flask. After 1,3-cyclohexadiene (320 mg, 4.0 mmol) was added to the solution, the solution was vigorously stirred for 4 h at 70 °C. The color of the solution changed from red to purple. After the solvent and remaining 1,3-cyclohexadiene were removed under reduced pressure, the residual solid was dissolved in 2 mL of pentane. The residual solid was then purified by column chromatography on alumina (Merck, Art. No. 1097) with pentane. Removal of the solvent under reduced pressure afforded a 0.199 g amount of 3 as a purple crystalline solid (82% yield). A thin platelike crystal used for the diffraction studies was prepared from the cold pentane solution of 3 stored at -30 °C. ¹H NMR (400 MHz, 23 °C, benzene- d_6): δ -22.88 (m, 1H, RuH), -9.00 (d, J_{H-H} = 4.8 Hz, 1H, RuH), 1.22 (m, 2H, -CHH^{endo}-), 1.77 (s, 30H, C₅Me₅), 2.14 (m, 2H, -CH^{exo}H-), 3.43 (m, 2H, -CH=CH-CH₂-), 4.98 (m, 2H, -CH= CH-CH₂-). ¹³C NMR (100 MHz, 23 °C, benzene- d_6): δ 12.0 (q, J_{C-H} = 127 Hz, C_5Me_5), 24.4 (t, J_{C-H} = 126 Hz, -CH=CH- CH_2 -), 62.9 (d, J_{C-H} = 159 Hz, -CH=CH- CH_2 -), 65.7 (d, J_{C-H} = 154 Hz, -CH=CH-CH₂-), 86.1 (s, C₅Me₅). IR (KBr): 893, 1020, 1112, 1163, 1193, 1370, 1443, 1460, 1480, 2820, 2890, 2942, 2960, 3013 (cm⁻¹). Anal. Calcd for C₂₆H₄₀Ru₂: C, 56.26; H, 7.27. Found: C, 56.20; H, 7.22.

Reaction of Cp*Ru(\mu-H)₄RuCp* (1) with Benzene. Benzene (2 mL) and diruthenium tetrahydrido complex 1 (37.8 mg, 79.3 μ mol) were charged in a reaction flask. The solution was vigorously stirred for 3 days at 70 °C. After the solvent was removed under reduced pressure, the residual solid was dissolved in 1 mL of pentane. The residual solid was then purified by column chromatography on alumina (Merck, Art. No. 1097) with pentane. After the first purple band was collected, the solvent was removed under reduced pressure. A 26.9 mg amount of 3 was obtained as a purple crystalline solid (61% yield).

Reaction of Cp*Ru(μ -H)₄RuCp* (1) with Benzene- d_6 . Benzene- d_6 (0.5 mL), diruthenium tetrahydrido complex 1 (8.7 mg, 18.2 μ mol), and cyclooctane (0.5 μ L) as an internal standard were charged in an NMR tube equipped with a Teflon valve. The solution was heated at 70 °C in an NMR probe. Due to rapid scrambling of deuterium of benzene- d_6 into the hydrido position, all of the signal except for the Cp* signal was gradually diminished. Concentrations of 1- d_4 and 3- d_{10} were evaluated by the intensity of the Cp* signals. The ratio between 1- d_4 and 3- d_{10} reached ca. 1:17 after 72 h heating and became steady. At the same time, other signals for Cp* groups were found at δ 2.03 and 1.90 ppm, which were assignable to triruthenium pentahydrido complex {Cp*Ru- $(\mu$ -H)}₃(μ_3 -H)₂ and tetraruthenium hexahydrido complex (Cp*Ru)₄(H)₆, respectively. On the basis of intensities of the Cp* signals, the yields of 1, 3, [Ru₃], and [Ru₄] were estimated at 4.5, 75.8, 7.1, and 10.1%, respectively.

Thermolysis of {Cp*Ru(μ -H)}₂(μ - η^2 : η^2 -C₆H₈) (3) under 1 atm of Dihydrogen Atmosphere. THF- d_8 (0.4 mL), μ -cyclohexadiene complex 3 (9.0 mg, 13.6 μ mol), and cyclooctane (0.5 μ L) as an internal standard were charged in an NMR tube equipped with a Teflon valve. After the NMR tube was degassed, the tube was filled with 1 atm of dihydrogen. The solution was heated at 40 °C for 30 h. The ¹H NMR spectrum of this solution showed the formation of diruthenium tetrahydrido complex 1 (92%) as well as benzene (90%).

Preparation of μ - η^2 -Cyclohexenyl Complexes {Cp*Ru-(CN^tBu)}₂(μ -H)(μ - η^2 -C₆H₉) (6). Pentane (10 mL) and μ -cyclohexadiene complex 3 (26.9 mg, 0.049 mmol) were charged in a reaction flask. After *tert*-butylisocyanide (0.15 mL, 1.5 mmol) was added to the

solution, the solution was vigorously stirred for 8 h at 40 °C. The color of the solution changed from purple to orange. The solvent was then removed under reduced pressure. The residual solid was dissolved in 2 mL of pentane. The residual solid was then purified by column chromatography on alumina (Merck, Art. No. 1097) with pentane. Removal of the solvent under reduced pressure afforded an orange residual solid including 6 with a small amount of 7. Recrystallization from the pentane solution of the solid stored at -30 °C gave 6 as an orange crystal (30.7 mg, 88% yield) and small amount of 7 as a red crystal. ¹H NMR of **6** (400 MHz, 23 °C, benzene- d_6): δ –13.57 (s, 1H, RuH), 0.98 (m, 1H, μ - η^2 -C₆H₉), 1.10 (s, 9H, ^tBuNC), 1.27 (s, 9H, ^tBuNC), 1.36–1.54 (m, 2H, μ - η^2 -C₆H₉), 1.84 (s, 15H, C₅Me₅), 2.05 (s, 15H, C_5Me_5), 2.34 (m, 1H, μ - η^2 - C_6H_9), 2.53 (m, 1H, μ - η^2 - C_6H_9), 2.70–2.80 (m, 2H, μ - η^2 -C₆H₉), 3.87 (m, 1H, μ - η^2 -C₆H₉), the signal derived from one of the methylene proton of the μ -cyclohexenyl ligand is obscured by the Cp* signal appearing at δ 2.05 ppm. ¹³C NMR (100 MHz, 23 °C, benzene- d_6): δ 4.3 (d, J_{C-H} = 138 Hz, Ru–CH–), 11.0 (q, J_{C-H} = 126 Hz, C_5Me_5), 12.0 (q, J_{C-H} = 125 Hz, C_5Me_5), 23.2 $(t, J_{C-H} = 128 \text{ Hz}, -CH_2-), 30.6 (t, J_{C-H} = 128 \text{ Hz}, -CH_2-), 31.9 (q,$ $J_{\rm C-H}$ = 128 Hz, (CH₃)₃CNC), 32.4 (t, -CH₂-), 33.3 (q, $J_{\rm C-H}$ = 129 Hz, (CH₃)₃CNC), 43.4 (d, $J_{C-H} = 156$ Hz, -CH=CH-), 55.0 $((CH_3)_3CNC)$, 59.3 (d, $J_{C-H} = 152$ Hz, -CH=CH-), 92.1 (s, C_5Me_5), 92.9 (s, C₅Me₅), 172.3 ((CH₃)₃CNC), 203.3 ((CH₃)₃CNC), only one signal for the quaternary carbon of the tert-butyl groups was observed at δ 55.0 ppm. This was probably due to the coincidence of the chemical shifts of the two signals. IR (KBr disk): 747, 813, 888, 1027, 1202, 1363, 1455, 1838 (ν (CN)), 2045 (ν (CN)), 2817, 2897, 2974 (cm⁻¹). Anal. Calcd for C₃₆H₅₈N₂Ru₂: C, 59.97; H, 8.11; N, 3.88. Found: C, 59.63; H, 8.11; N, 3.89. ¹H NMR of 7 (400 MHz, 23 °C, benzene- d_6): δ 1.13 (s, 18H, ^tBuNC), 1.16 (s, 18H, ^tBuNC), 1.79 (s, C₅Me₅).

Preparation of μ -Cyclohexylidene Complex {Cp*Ru(CO)}₂- $(\mu$ -C₆H₁₀) $(\mu$ -CO) (8). THF (5 mL) and μ -cyclohexadiene complex 3 (80.8 mg, 0.15 mmol) were charged in a reaction flask. After the flask was degassed, 1 atm of CO was introduced into the flask. The solution was heated at 50 °C for 15 h. The color of the solution changed from purple to yellow. The solvent was then removed under reduced pressure. The ¹H NMR spectrum of the residual solid showed that complexes 8 and $\{Cp^*Ru(CO)(\mu-CO)\}_2$ (9) were formed in a 47:53 ratio. Characterization of 9 was carried out by comparing its ¹H NMR and IR spectra with that of authentic samples (δ 1.71 (s, 30H, C₅Me₅), ν (CO) = 1748 and 1934 cm⁻¹). The residue was extracted three times with 5 mL of pentane to remove 9. After the combined solution was condensed to 2 mL, the solution was purified by column chromatography on alumina (Merck, Art. No. 1097) with pentane. The first yellow band including 8 was collected, and removal of the solvent under reduced pressure afforded a 23.0 mg amount of 8 as a yellow crystalline solid (24% yield). A yellow single crystal used for the diffraction studies was prepared by the slow evaporation of the THF solution of 8 stored at 25 °C. ¹H NMR (400 MHz, 23 °C, benzene- d_6): δ 1.75 (s, 30H, C₅Me₅), 1.85–2.00 (m, 4H, μ -C₆H₁₀), 2.02-2.12 (m, 2H, μ-C₆H₁₀), 3.17 (m, 2H, μ-C₆H₁₀), 3.25 (m, 2H, μ- C_6H_{10}) ppm. ¹³C NMR (100 MHz, 23 °C, benzene-*d*₆): δ 10.3 (q, J_{C-H} = 127 Hz, C_5Me_5), 28.1 (t, J_{C-H} = 136 Hz, $-CH_2-$), 30.5 (t, J_{C-H} = 126 $Hz_{1} - CH_{2} - J_{1}, 60.0 (t_{1} J_{C-H} = 115 Hz_{1} - CH_{2} - J_{1}, 102.1 (s_{1} C_{5} Me_{5}), 181.3$ (s, μ-C), 204.0 (s, CO), 254.7 (μ-CO) ppm. IR (KBr): 800, 857, 1007, 1025, 1111, 1257, 1381, 1442, 1473, 1769 (v(CO)), 1911(v(CO)), 2855, 2913, 2961, 2989 (cm⁻¹). Anal. Calcd for C₂₉H₄₀O₃Ru₂: C, 54.53; H, 6.31. Found: C, 54.17; H, 6.28.

Preparation of μ - η^2 : η^2 -Cyclopentadiene Complex {Cp*Ru-(μ -H)}₂(μ - η^2 : η^2 -C₅H₆) (10). Toluene (5 mL) and diruthenium tetrahydrido complex 1 (0.094 g, 0.20 mmol) were charged in a reaction flask. Cyclopentadiene (0.1 mL, 1.27 mmol) was added to the solution at 25 °C. The solution was vigorously stirred for 4 h at 70 °C. The color of the solution changed from red to brown. After the solvent and remaining cyclopentadiene were removed under reduced pressure, the residual solid was dissolved in 2 mL of toluene. The residual solid was then purified by column chromatography on alumina (Merck, Art. No. 1097) with toluene, and the brown band was collected. After removal of the solvent under reduced pressure, complex **10** was obtained as a brownish solid (0.065 g, 60% yield). A needle-like orange crystal used for the diffraction studies was prepared from the cold pentane solution of **10** stored at $-30 \,^{\circ}$ C. ¹H NMR (400 MHz, 23 $^{\circ}$ C, benzene- d_6): $\delta -22.32$ (m, 1H, RuH), -9.91 (d, $J_{HH} = 4.0 \,\text{Hz}$, 1H, RuH), 1.69 (s, 30H, C_5Me_5), 2.45 (m, 1H, $-CH^{endo}H-$), 3.75 (m, 1H, $-CHH^{exo}-$), 4.19 (m, 2H, $-CH=CH-CH_2-$), 5.13 (m, 2H, $-CH=CH-CH_2-$). ¹³C NMR (100 MHz, 23 $^{\circ}$ C, benzene- d_6): $\delta \,$ 11.3 (q, $J_{C-H} = 127 \,\text{Hz}, C_5Me_5$), 52.6 (dd, $J_{C-H} = 137, 115 \,\text{Hz} - CH=CH-CHH'-$), 70.4 (d, $J_{C-H} = 162 \,\text{Hz}, -CH=CH-CH \,\text{H}'-$), 71.4 (d, $J_{C-H} = 165 \,\text{Hz}, -CH=CH-CH \,\text{H}'-$), 86.7 (s, C_5Me_5). IR (KBr): 869, 903, 985, 1022, 1098, 1135, 1159, 1260, 1317, 1422, 1449, 2777, 2893 (cm⁻¹). Anal. Calcd for $C_{25}H_{38}Ru_2$: C, 55.53; H, 7.08. Found: C, 55.36; H, 7.17.

Preparation of μ - η^2 : η^2 -Cycloheptadiene Complex {Cp*Ru- $(\mu-H)_{2}(\mu-\eta^{2}:\eta^{2}-C_{7}H_{10})$ (11). Toluene (5 mL) and diruthenium tetrahydrido complex 1 (0.081 g, 0.17 mmol) were charged in a reaction flask. Cycloheptatriene (0.1 mL, 0.88 mmol) was added to the solution at 25 °C. The solution was vigorously stirred for 18 h at 70 °C. The color of the solution changed from red to purple. After the solvent and remaining cyclopentadiene were removed under reduced pressure, the residual solid was dissolved in 2 mL of toluene. The residual solid was then purified by column chromatography on alumina (Merck, Art. No. 1097) with toluene, and a purple band was collected. After removal of the solvent under reduced pressure, complex 11 was obtained as a purple solid (0.067 g, 70% yield). A needle-like red crystal used for the diffraction studies was prepared from the pentane solution of 11 stored at 20 °C. ¹H NMR (400 MHz, 23 °C, benzene- d_6): δ –22.84 (m, 1H, RuH), –8.39 (d, $J_{\rm HH}$ = 4.8 Hz, 1H, RuH), 0.06 (m, 1H, -CHH'-), 1.25 (m, 1H, -CHH'-), 1.70 (m, 2H, -CHH'-), 1.72 (s, 30H, C₅Me₅), 1.94 (m, 2H, -CHH'-), 2.45 (m, 1H, -CH^{endo}H-), 3.75 (m, 1H, -CHH^{exo}-), 3.11 (m, 2H, -CH=CH- CH_2 -), 5.09 (m, 2H, $-CH=CH-CH_2$ -). ¹³C NMR (100 MHz, 23 °C, benzene- d_6): δ 12.0 (q, J_{C-H} = 126 Hz, C_5Me_5), 30.1 (t, J_{C-H} = 124 Hz, $-CH_2-$), 30.5 (t, $J_{C-H} = 124$ Hz, $-CH_2-$), 68.3 (d, $J_{C-H} = 154$ Hz, -CH=CH-CH₂-), 74.8 (d, J_{C-H} = 148 Hz, -CH=CH-CH₂-), 85.3 (s, C5Me5).

Thermolysis of μ -η²:η²-Cyclopentadiene Complex 10 in Benzene-d₆. Benzene-d₆ (0.4 mL) and μ -η²:η²-cyclopentadiene complex 10 (6.5 mg, 12 µmol) were charged in an NMR tube with hexamethyldisiloxane as an internal standard. The NMR tube was heated at 70 °C for 2 h. The ¹H NMR spectrum of the solution showed that 94% of 10 was consumed and Cp*RuCp (12) was formed in 45% yield. The yield was estimated from the signal intensity of the Cp* group compared with that of the internal standard. ¹H NMR (400 MHz, 23 °C, benzene-d₆): δ 1.92 (s, 15H, C₅Me₅), 4.18 (s, 5H, C₅H₅) ppm. ¹³C NMR (100 MHz, 23 °C, benzene-d₆): δ 12.4 (q, J_{C-H} = 127 Hz, C₅Me₅), 72.4 (doublets of quintet, J_{C-H} = 174, 7 Hz, C₅H₅), 84.9 (s, C₅Me₅) ppm. ¹H NMR (400 MHz, 23 °C, CD₃Cl): δ 1.96 (s, 15H, C₅Me₅), 4.17 (s, 5H, C₅H₅) ppm.

ASSOCIATED CONTENT

Supporting Information. Results of NMR simulations on 3 and 10, results of X-ray diffraction studies of 7, as well as crystallographic files including CIF files of 3, 6, 7, 8, 10, and 11 are available free of charge via the Internet at http://pubs.acs.org.

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(19) In the ¹H NMR spectrum of the crude mixture, a Cp* signal except for that of **12** was observed at δ 1.83 ppm. Becase the isolation of this compound was not successful and other signals derived from this species were not observed in the NMR spectrum, we could not characterize this species at present.

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