Mechanistic Study on Cp- and Cp*Ru$^+$-Mediated Cycloaddition between Conjugated Dienes and Acetylene

Katsuyuki Masuda, Hironobu Ohkita, Shigeru Kurumatani, and Kenji Itoh*

Department of Materials Science, Toyohashi University of Technology, Tenpaku-cho, Toyohashi, Aichi 441, Japan

Received December 14, 1992

When Cp*RuCl(η^4-diene), where diene = butadiene (**1a**) or 1,3-pentadiene (**1b**), was treated with excess acetylene in the presence of silver triflate, [Cp*Ru{η^2,η^4-C_6H_7(CH=CH_2)}]$^+$ (**3a**) and [Cp*Ru{η^2,η^4-C_6H_6(CH_3)(CH=CH_2)}]$^+$ (**3b**) were formed as predominant products in 84 and 71% yields, respectively. On the basis of the distribution patterns of the deuteration experiments with C_2D_2, the new hydrocarbon ligand was found to be generated by the following sequence of steps; (1) [4 + 2] cycloaddition of acetylene and the coordinated diene ligand, (2) C—H activation to form a Ru(IV) cyclohexadienyl–hydride intermediate, (3) insertion of the second acetylene molecule into the formed Ru(IV)—H bond, and (4) the resultant vinyl ligand coupling with the cyclohexadienyl ligand. Dehydrogenation or methane elimination from the [4 + 2] cycloadducts, 1,4-cyclohexadiene intermediate, as well as cyclic trimerization of acetylene, resulted in the formation of stable [Cp*Ru(η^6-arene)]OTf (**2a** and **2b**) as minor products (10–22%). Alternatively, the formation of the cationic arene complexes (**2a** and **2b**, **2d** or **2e**) became predominant, and that of 1:2 adducts was completely suppressed, when Cp*RuCl(η^4-isoprene) (**1c**) or CpRuCl(η^4-diene) complexes, diene = butadiene (**1d**) and isoprene (**1e**), were employed.

Introduction

Coordinated alkynes have been reported to show a wide range of reactivities in organoruthenium complex chemistry.[1] Terminal alkynes involving alkyl, aryl, or alkoxycarbonyl substituents have been found to induce insertion reactions in a variety of chloro- or hydrido–ruthenium(II) complexes.[2b,c,3] The other two characteristic reactions of terminal alkynes are acetylide formation via C–H bond activation[4,5] and the generation of vinylidene species by way of the 1,2-hydrogen shift.[5,6] The latter recently proved to play the most important role in Yamazaki's unusual ruthenium-catalyzed dimerization of *tert*-butylacetylene,[7] which had been reported several years ago, to furnish the corresponding 1,2,3-butatriene.[8] Internal alkynes have also been reported to undergo insertion reactions.[2b,c,9]

Another representative transformation of coordinated alkynes is the formation of metallacycle complexes with other unsaturated substrates.[2a,b,9] The reaction has been applied to a ruthenium-catalyzed codimerization between internal acetylenes and methyl acrylate by Mitsudo and co-workers.[10]

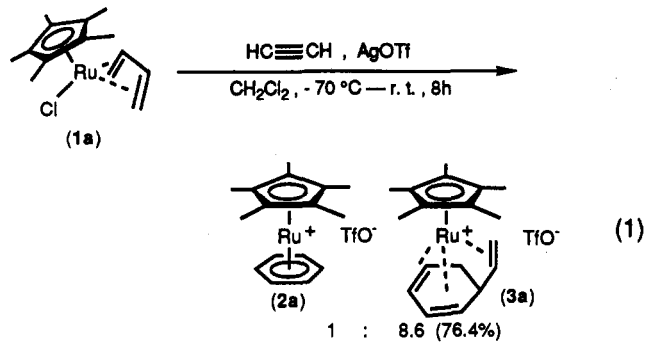
There have been, however, a few studies in organoruthenium chemistry of C_2H_2 itself, expecting examples of insertion reactions.[2b,5c,11] Recently, Lomprey and Selegue reported the formation of a vinylidene complex from coordinated acetylene.[12] We describe herein a new type of ruthenium-mediated cotrimerization between a coordinated diene and two acetylene molecules by means of the (C_5Me_5)Ru$^+$ fragment and [4 + 2] cyclodimerization as an extension of our previous work on the oligomerization of conjugated dienes.[13]

Results and Discussion

(1) Reaction of Coordinated Dienes with Alkynes. Cp*RuCl(η^4-butadiene) (**1a**) was treated with silver triflate (trifluoromethanesulfonate; TfO) at −78 °C in dichloromethane, and an excess of acetylene (1 atm) was introduced at this temperature. Two products were detected in the ^{1}H-NMR spectra which showed the presence of two Cp* peaks at δ 1.86 and 2.03 ppm. One of the products was identified as the known [Cp*Ru(η^6-benzene)]OTf (**2a**) by comparing its spectral data with independently prepared authetic material.[14] The forma-

(1) Davis, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1.
(2) (a) Torres, M. R.; Santos, A.; Ros, J.; Solans, X. *Organometallics* **1987**, *6*, 1091. (b) Torres, M. R.; Vegas, A.; Santos, A. *J. Organomet. Chem.* **1987**, *326*, 413. (c) Torres, M. R.; Vegas, A.; Santos, A. *J. Organomet. Chem.* **1986**, *309*, 169.
(3) Xue, Z.; Sieber, W. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1990**, *112*, 1825.
(4) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 621. Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.
(5) (a) Bozec, H. L.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768. (b) Bray, J. M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1989**, 589. (c) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.
(6) Devanne, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 641.
(7) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604.
(8) Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1976**, 541. Wakatsuki, Y.; Satoh, Y.; Yamazaki, H. *Chem. Lett.* **1989**, 1585.
(9) Bruce, M. I.; Gardner, C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 906. Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106. Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1971**, 852.
(10) Mitsudo, T.; Zhang, S.; Nagao, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 598.
(11) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165.
(12) Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518.
(13) Masuda, K.; Nakano, K.; Fukahori, T.; Nagashima, H.; Itoh, K. *J. Organomet. Chem.* **1992**, *428*, C21.
(14) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2243. Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 5671.

0276-7333/93/2312-2221$04.00/0



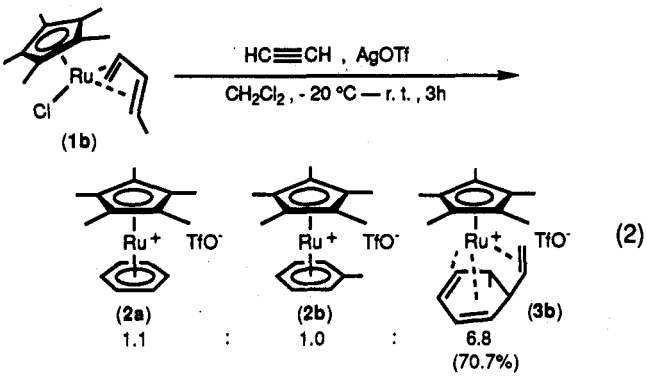
(1)

tion of **2a** is explained by way of [4 + 2] cycloaddition followed by the elimination of a hydrogen molecule from the intermediate 1,4-cyclohexadiene complex.[15] The other major product was found to be a 5-vinyl-1,3-cyclohexadiene complex (**3a**) on the basis of its elemental analysis and the following spectroscopic evidence.

The ^{1}H-NMR spectrum of **3a** exhibited one terminal vinyl (δ 3.03, 3.16, 3.35 ppm), four olefin (3.41, 3.62, 5.07, 5.12 ppm), the methyne adjacent to the vinyl unit (3.54 ppm), and one methylene (0.69, 0.82 ppm) proton resonances. In addition, ^{13}C-NMR spectra indicated one methylene (47.0 ppm) and five methyne olefin carbon signals (42.3, 47.5, 70.1, 81.5, 85.5 ppm) and methylene (13.9 ppm) and methyne (27.6 ppm) alicyclic carbon signals, together with the Cp* peaks at 9.86 and 96.6 ppm. The ligand framework of **3a**, 5-vinyl-1,3-cyclohexadiene, is composed of two acetylene and one butadiene molecules.

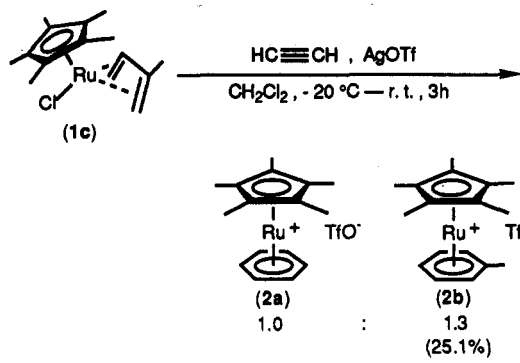
The relative ratio of these two products was estimated to be **2a**:**3a** = 11:89 from the relative intensity of Cp* signals in the ^{1}H-NMR spectra. At higher initial temperatures (above −40 °C), the relative amount of **3a** was decreased, although the total yield of **3a** and **2a** was slightly increased (Table I).

The reaction between Cp*RuCl(η^4-1,3-pentadiene) (**1b**) and acetylene in the presence of AgOTf at −20 °C furnished a mixture of the 1:2 cycloaddition complex (**3b**; 71%), the



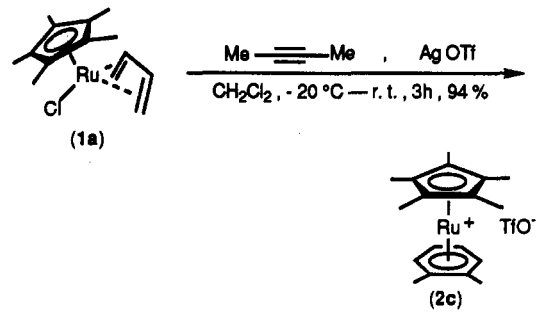
(2)

toluene complex **2b**, and the benzene complex **2a** in the ratio 6.8:1.0:1.1. The formation of **2a** was surprising. In order to shed light on the mechanistic aspects of the formation of the benzene complex **2a**, the reaction of [Cp*Ru(η^4-isoprene)]$^+$ with acetylene was studied. When Cp*RuCl(η^4-isoprene) (**1c**) was sequentially treated with AgOTf and with acetylene (1 atm) between −20 °C and ambient temperature, the only products were cationic benzene complexes **2a** and a toluene complex **2b** in a 1.0:1.3 molar ratio. However, the 1:2 cycloaddition product,



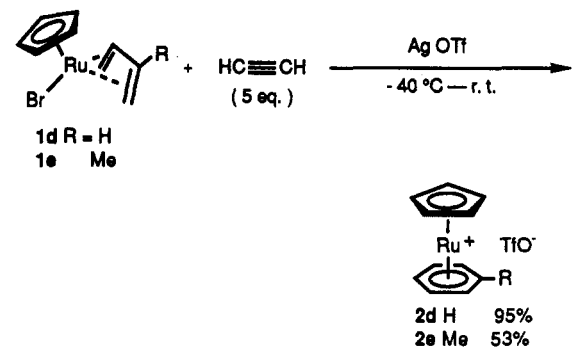
(3)

the vinylcyclohexadiene complex, was never found in the product. Alternatively, [Cp*Ru(η^4-butadiene)]$^+$ selectively afforded the *o*-xylene complex [Cp*Ru(η^6-*o*-xylene)]OTf (**2c**) in the reaction with 2-butyne (94%).



(4)

Changing the C_5Me_5 (Cp*) ligand to C_5H_5 (Cp) also inhibited completely the formation of a 5-vinyl-1,3-cyclohexadiene complex such as **3a** or **3b**. For instance, when CpRuCl(η^4-butadiene) (**1d**) was treated with silver



(5)

triflate followed by introduction of acetylene (5 equiv at 1 atm) at −20 °C, only the benzene complex **2d** was isolated in 95% yield. Similarly, the reaction of the coordinated isoprene in CpRuCl(η^4-isoprene) (**2e**) with acetylene afforded only the toluene complex **2e** (53%).

(2) Mechanistic Study. 5-Vinyl-1,3-cyclohexadiene complex **3a**, a 1:2 adduct of the butadiene complex and acetylene, can be produced by way of two possible routes as depicted in Scheme I.

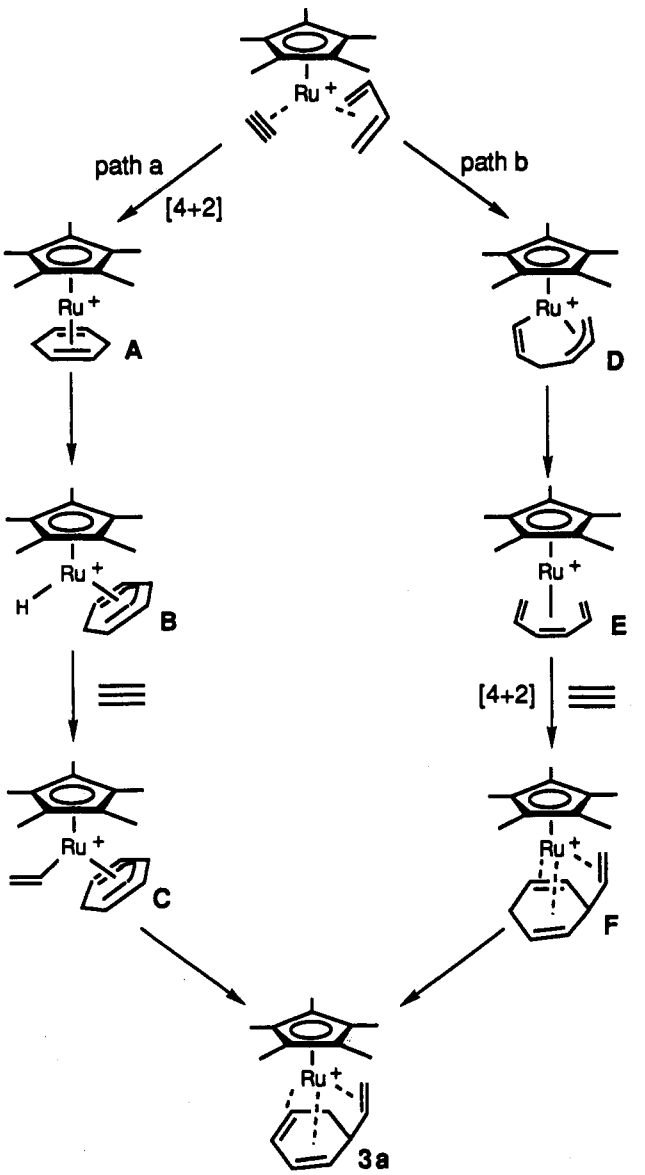
The first mechanism involves a ((1–5-η)-cyclohexadienyl)ruthenium(IV) hydride as the key intermediate (path a). That is, a ruthenium-mediated [4 + 2] cycloaddition between the coordinated diene and acetylene furnishes a 1,4-cyclohexadiene complex (A), which is converted to a 1–5-η-cyclohexadienyl hydride intermediate (B). Insertion of the second acetylene into the Ru–H bond to give C followed by the reductive coupling between the vinyl group and the terminal position of the η^5-cyclohexadienyl ligand

(15) Rondon, D.; Chaudret, B.; He, Xiao-D.; Labroue, D. *J. Am. Chem. Soc.*, **1991**, *113*, 5671.

Table I. Conversion of 2a and 3a at Various Temperatures

reacn condition		yield (%)		molar ratio	
temp (°C)	time (h)	2a	3a	2a	3a
−70 to room temp	8	9.0	76.4	10.6	89.4
−40	2	7.4	61.6	11.0	89.0
−40 to room temp	8	11.9	79.9	13.1	86.9
−40 to room temp	3.5	17.3	70.3	19.7	80.3
−20 to room temp	3	20.9	69.5	22.9	77.1

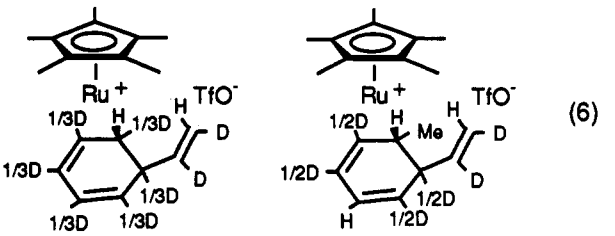
Scheme I



from the resultant Ru(IV) intermediate gives the final vinylcyclohexadiene framework.

Alternatively, a key intermediate of the second mechanistic possibility is a 1,3,5-hexatriene complex (path b, E). This intermediate is formed by the coupling both ends of the coordinated butadiene and an entering alkyne to give a metallacycle intermediate (D), which gives a η^6-1,3,5-hexatriene intermediate (E) by a 1,3-hydrogen migration. A coordinatively unsaturated site can be generated by dissociation of one vinyl part of the η^6-hexatriene ligand, and this site is occupied by the second acetylene molecule to furnish $[Cp^*Ru(\eta^4\text{-}C_6H_8)(\eta^2\text{-}C_2H_2)]^+$. [4 + 2] cycloaddition between coordinated η^4 and η^2 ligands gave a 3-vinyl-1,4-cyclohexadiene intermediate (F), which can isomerize to **3a**.

In order to distinguish between the above two pathways for formation of the particular 1:2 adduct complex (**3a** and **3b**), the following deuterium-labeled experiments were undertaken with C_2D_2. The distribution of the deuterium atoms of the resultant vinylcyclohexadiene complex is shown in eq 6. When deuterated acetylene was employed,



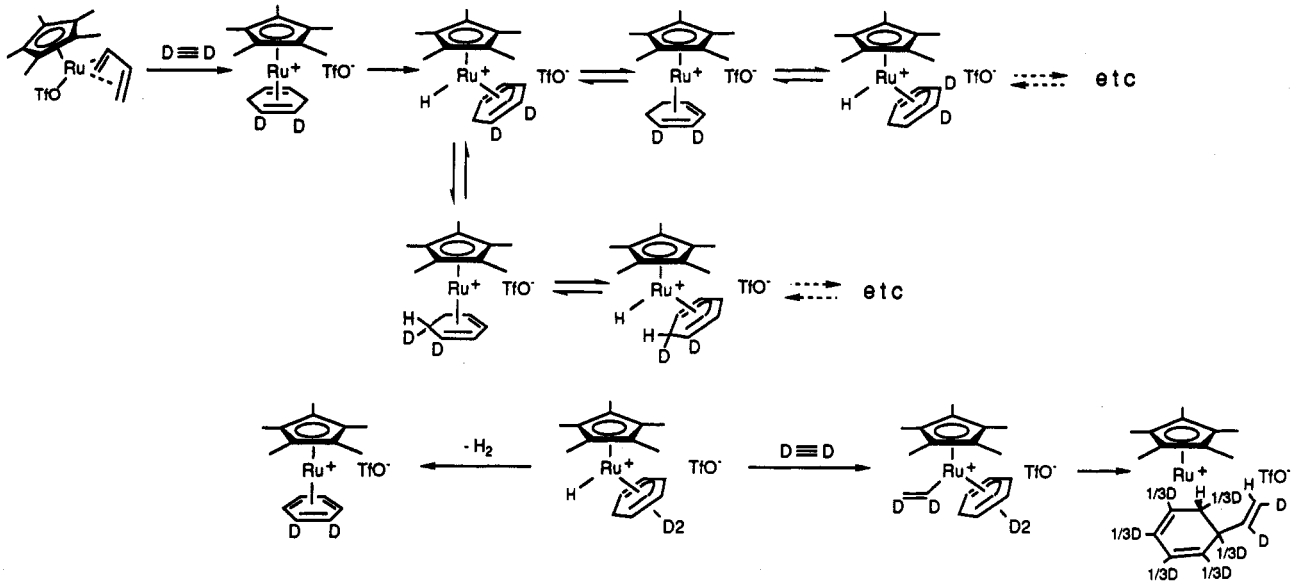
(6)

the relative intensity of the resonances of the 5-vinyl-1,3-hexadiene ligand in **3a** was four protons less in total than in the C_2H_2 product, measured relative to the Cp* peak intensity. Two detuerium atoms were specifically introduced at the pendant vinyl unit. The proton resonances at δ 3.03 and 3.16 in **3a** disappeared when C_2D_2 was used. In addition the vinyl doublet at δ 3.35 in **3a** turned to a broad singlet by loss of a trans coupling (J = 12.7 Hz). This result suggests two deuterium atoms were introduced in 1,2-cis positions in the pendant vinyl group. The remaining two deuterium atoms were scrambled among the six-membered-ring carbons in the cyclohexadienyl moiety (33 ± 3% D for six-membered-ring carbons). This is consistent with ^{2}D NMR measurements which indicated the appearance of signals corresponding to the disappeared proton resonance positions. Such deuterium distribution strongly supports that the cyclohexadienyl hydride intermediate (B) is a key intermediate, as shown in path a in Scheme I. Furthermore, the specific introduction of two deuterium atoms in the pendant vinyl group is not consistent with the intermediate **E** in path b, because its symmetric structure should result in incorporation of 50% deuterium atoms in the vinyl group of the final product. Consequently, this finding is also indicative of path a being predominant for the formation **3a**.

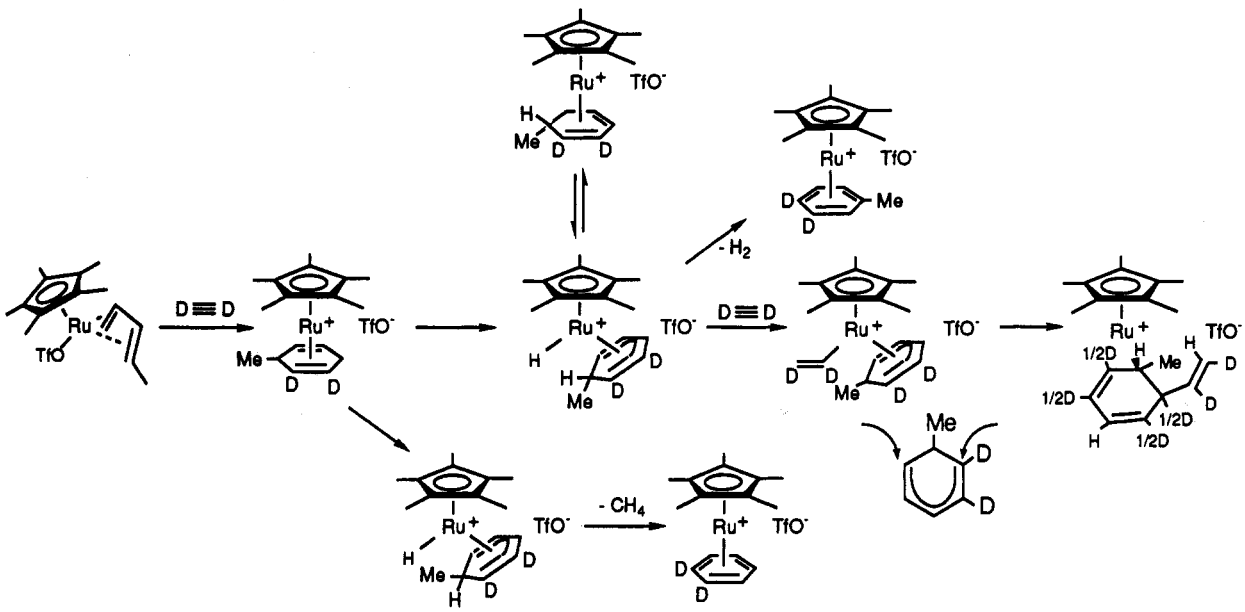
From these facts, Scheme II summarizes the mechanism of the deuterium scrambling patterns in these ligands. Scrambling of the deuterium in the six-membered ring was due to rapid and reversible isomerization of the (η^5-cyclohexadienyl)ruthenium(IV) hydride and the (1,3-cyclohexadiene)ruthenium(II) intermediates. It is noteworthy that the methylene proton at C6 which faces the Cp*Ru moiety in the six-membered ring was not deuterated in the complexes. These results indicate that prototropic isomerization takes place not by deuterium migration but by hydrogen migration. During reversible C–H bond activation, the deuterium atoms were not activated. The pendant vinyl substituent of the 5-vinyl-1,3-cyclohexadiene ligands in the 1:2 adducts (**3a**) was formed at the final step by the hydride insertion of the second acetylene molecule into the cyclohexadienyl hydride Ru(IV) intermediate. This may be the first example of the insertion of a Ru(IV)–H bond to our knowledge. Subsequent reductive coupling between the vinyl group and either hexadienyl ends furnished the final 1:2 adducts.[16]

(16) Review of insertion reactions: Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1986**, *309*, 169.

Scheme II



Scheme III



In the case of the 1,3-pentadiene analogue (**3b**), whereas two deuterium atoms were similarly introduced in the vinyl unit, the remaining two deuterium atoms were selectively introduced only at the 1,2,4,5-positions of the six-membered ring (49 ± 9% D). This deuterium scrambling pattern (eq 6) in **3b** was explained by reductive coupling between the vinyl and the cyclohexadienyl ligand taking place in equal probability only in both terminals. In the case of **3b**, however, prototropic isomerization was inhibited because of severe steric interaction of the methyl group with the Cp* ligand (Scheme III).

On the other hand, the reaction of coordinated isoprene with acetylene in the Cp system and coordinated butadiene with dimethylacetylene in **1c** yielded selectively the toluene **2e** and the *o*-xylene **2c** complexes, respectively. Thus cyclotrimerization of three acetylene molecules to the benzene complex **2a** did not occur in these cases. It is reasonable to conclude that CpRu(η^6-arene)$^+$ complexes (**2d**, **2e**) and Cp*Ru(η^6-*o*-xylene)$^+$ (**2c**) were produced by [4 + 2] cycloaddition of the coordinated diene and the alkynes followed by elimination of a hydrogen molecule.

Reactions of the Cp*Ru derivatives of the methyl-substituted dienes, **1b** and **1c**, gave a mixture of the benzene **2a** and the toluene **2b** complexes. It is necessary to consider alternative pathways to explain in particular the formation of **2a**. There are two plausible candidates; (1) simple cyclotrimerization of acetylenes and (2) elimination of methane from a methylcyclohexadienyl intermediate. The latter type of C–C bond activation has already been reported by Chaudret and co-workers in the case of a methylcyclohexadiene complex of "Cp*Ru$^+$".[15]

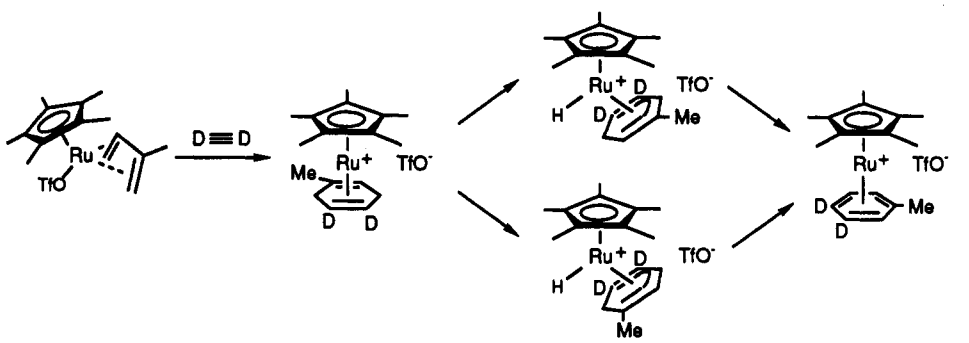
In order to discriminate between these two mechanisms and the above mentioned [4 + 2] pathway, experiments using Cp*RuCl(η^4-diene) and deuterated acetylene (99.8% D) were undertaken. The results are summarized in Table II. In the reaction of [Cp*Ru(η^4-butadiene-d_0)]$^+$ with C_2D_2 (entry 1), the relative intensity of the $C_6D_{6-n}H_n$ ligand was estimated to be n = 1.47 based on the Cp* methyl groups. The above value suggests that **2a** should be formed by way of either [4 + 2] cycloaddition (37%) of C_4H_6 and C_2D_2 or cyclotrimerization (63%) of three C_2D_2 molecules,

Table II. Reaction of [Cp*Ru(diene)]⁺ with C_2D_2[a]

entry	reacn	rel ratio: benzene-d_2	benzene-d_6	toluene-d_2	d_4 1:2 adduct
1	Cp*RuCl(butadiene)–AgOTf–acetylene-d_2	1	1.72		29.5
2	Cp*RuCl(1,3-pentadiene)–AgOTf–acetylene-d_2	1	5.00	6.48	42.3
3	Cp*RuCl(isoprene)–AgOTf–acetylene-d_2	0	3.94	1	

[a] Relative ratios were determined by ^{1}H-NMR spectra: the relative intensity of each aromatic signal to the methyl proton signals of the Cp* ligands.

Scheme IV



if one postulates the arene complex was composed of only $[Cp^*Ru(C_6H_4D_2)]^+$ and $[Cp^*Ru(C_6D_6)]^+$.

Trimerization of acetylene also took place in the case of the coordinated 1,3-pentadiene to give a benzene-d_6 complex. In this case, however, the benzene-d_2 complex was also formed by the methane elimination, with a benzene-d_6:benzene-d_2 ratio of 5:1. Surprisingly, no methane elimination was observed in the isoprene complex to give only benzene-d_6 (acetylene trimerization) and toluene-d_2 ([4 + 2] cycloaddition) complexes.

These results indicate that the selectivity of methane-forming C–C activation is determined by the position of the methyl group in the [4 + 2] cycloaddition products. In the case of 1,3-pentadiene complex **1b**, C–C bond activation occurred with elimination of methane only from a minor [4 + 2] cycloadduct with the methyl group oriented toward the metal center, as shown in the bottom of the Scheme III. Alternatively, the methyl group of 1-methyl-1,4-cyclohexadiene intermediates formed in the case of isoprene was not located at the position to be activated, as shown in Scheme IV. The elimination of a hydrogen molecule from the directly produced 1- or 2-methylcyclohexadienyl hydride intermediates takes place much faster than the prototropic isomerization by reversible C–H bond activation. Consequently, the hydride insertion of the acetylene becomes impossible.

Experimental Section

General Remarks. All reactions with organometallic compounds were carried out in an argon atmosphere. Ruthenium trichloride hydrate was purchased from NE Chemcat Corp. Dichloromethane was distilled from P_2O_5 and stored under an argon atmosphere. Other organic reagents were obtained commercially and used without further purification. The following spectrometers were used: NMR JEOL GX-2700 (270 MHz for ^{1}H and 67.8 MHz for ^{13}C, FT), Varian VXR-500S (500 MHz for ^{1}H); IR Japan Spectroscopic Co. A-3. Elemental analyses were carried out by the Microanalysis Center of Kyoto University. Deuterated acetylene, C_2D_2, was prepared by the hydration of CaC_2 with an excess of D_2O. Preparation of Cp*RuCl(η^4-diene) complexes were made by modification of methods reported by us[13] and others.[17]

Preparation of (η^5-Pentamethylcyclopentadienyl)(η^4-diene)chlororuthenium(II). Into a 30-mL round-bottomed flask was placed 21.3 mg of zinc powder (0.33 mmol) and $[Cp^*RuCl_2]_2$[18] (100 mg, 0.33 mmol). After the flask was cooled to ice temperature, methanol (10 mL) and diene (10 mmol) were added, and the reaction mixture was stirred for 20 min at this temperature. The reaction solution was filtered through Celite under dinitrogen and concentrated under reduced pressure. Chromatographic purification of the residue (SiO_2/CH_2Cl_2) gave the title complex as pale yellow crystals.

1a (diene = butadiene): ^{1}H-NMR (270 MHz, $CDCl_3$, TMS) δ 1.51 (2H, dd, J = 1.71, 10.25 Hz), 1.65 (15H, s), 3.28 (2H, dd, J = 8.55), 4.49 (2H, m).

1b (diene = isoprene): ^{1}H-NMR (270 MHz, $CDCl_3$, TMS) δ 1.38 (1H, dd, J = 1.95, 10.26 Hz), 1.51 (1H, s), 1.65 (15H, s), 2.00 (3H, s), 3.24 (1H, dd, J = 7.56), 3.34 (1H, s), 4.43 (1H, dd, J = 7.56, 10.26). Anal. Calcd for $C_{15}H_{23}ClRu$: C, 53.01; H, 6.82. Found: C, 53.07, H, 6.93.

1c (diene = 1,3-pentadiene): ^{1}H-NMR (270 MHz, $CDCl_3$, TMS) δ 1.40 (1H, dd, J = 1.96, 10.25 Hz), 1.62 (15H, s), 1.65 (3H, d, J = 0.97), 2.22 (1H, dt, J = 0.97, 10.26), 3.04 (1H, dd, J = 1.96, 6.84), 4.43 (1H, m), 4.57 (1H, dd, J = 5.37, 10.26). Anal. Calcd for $C_{15}H_{23}ClRu$: C, 53.01; H, 6.82. Found: C, 53.07; H, 6.83.

Reaction of (η^5-Pentamethylcyclopentadienyl)(η^4-1,3-butadiene)chlororuthenium(II) and Acetylene. Into a 100-mL round-bottomed flask was placed 100 mg of Cp*RuCl(butadiene) (**1a**; 0.307 mmol) and dichloromethane (44.8 mL). The flask was cooled to −70 °C in a dry-ice acetone bath, and 1.86 mL of an acetone solution (0.2 N) of silver triflate (0.37 mmol) was added. An argon atmosphere in the flask was changed to atmospheric pressure of acetylene. After this temperature was kept for 5 h, the temperature of the bath was raised to room temperature over period of 3 h. The reaction mixture was filtered through a Celite column under a dinitrogen stream, and then the filtrate was concentrated under reduced pressure. Recrystallization (CH_2Cl_2/Et_2O) gave the mixture of two complexes (**3a** and **2a**). ^{1}H-NMR analysis indicated that the yields of **3a** and **2a** were 84.4 and 9.7%, respectively.

[Cp*Ru{η^2,η^4-C_6H_7(CH=CH_2)}]OTf (**3a**): ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 0.69 (1H, dd, J = 3.91, 14.16 Hz, C6—H inside), 0.82 (1H, dd, J = 5.86, 14.16, C6—H outside), 1.86 (15H, s, Cp*), 3.03 (1H, ddd, J = 2.93, 7.81, 12.7, –C*H*=CH_2), 3.16 (1H, d, J = 7.81, cis vinyl), 3.35 (1H, d, J = 12.7, trans vinyl), 3.41 (1H, m, C4—H), 3.54 (1H, m, C5—H), 3.62 (1H, ddd, J = 1.95, 5.86, 7.33, C1—H), 5.07 (1H, ddd, J = 1.46, 4.89, 6.84, C3—H), 5.12

(17) Bosch, H. W.; Hund, Hans-U.; Nietlispach, D.; Salzer, A. *Organometallics* **1992**, *11*, 2087.

(18) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161. Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274.

(1H, dd, J = 4.89, 7.33, C2-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 9.86 (q, J = 129.1 Hz), 13.9 (t, J = 133.0), 27.6 (d, J = 150.6), 42.3 (d, J = 170.2), 47.0 (t, J = 164.3), 47.5 (d, J = 170.2), 70.1 (d, J = 164.3), 81.5 (d, J = 172.2), 85.5 (d, 174.1), 96.6 (s); IR 3050 cm^{-1} (w), 2900 (w), 1460 (m), 1380 (m), 1260 (s), 1220 (m), 1140 (s), 1020 (s), 730 (w), 635 (s), 570 (w), 515 (w). Anal. Calcd for $C_{19}H_{25}O_3SF_3Ru$: C, 46.43, H, 5.13. Found: C, 46.51; H, 5.01.

[Cp*Ru(η^6-benzene)]OTf (**2a**): ^{1}H-NMR (270 MHz, $CDCl_3$, TMS) δ 2.03 (15H, s), 5.86 (6H, s); ^{13}C-NMR (67.8 MHz, $CDCl_3$): δ 10.8 (q, J = 129.1 Hz), 87.2 (d, J = 176.0), 97.0 (s). Anal. Calcd for $C_{17}H_{21}O_3SF_3Ru$: C, 44.05; H, 4.57. Found: C, 44.12; H, 4.46.

Reaction of (η^5-Pentamethylcyclopentadienyl)(η^4-1,3-pentadiene)chlororuthenium(II) and Acetylene. The procedure for the reaction was similar to that described above. The reaction was performed from Cp*RuCl(1,3-pentadiene) (**1a**; 17.4 mg, 0.0513 mmol), silver triflate (1.2 equiv), and acetylene (1 atm) in dichloromethane (7.5 mL) (3 h, −20 °C to room temperature). ^{1}H-NMR analysis of the oily product indicated that **3a**, **2a**, and **2b** were formed in 70.7, 11.4, and 10.2% yields, respectively.

[Cp*Ru{η^2,η^4-$C_6H_6(CH_3)(CH{=}CH_2)$}]OTf (**3b**): ^{1}H-NMR (270 MHz, $CDCl_3$, TMS) δ 0.83 (3H, d, J = 7.32 Hz, C6—Me), 1.11–1.30 (1H, m, C6—H), 1.84 (15H, s, Cp*), 3.02 (1H, ddd, J = 2.93, 8.30, 12.7, -C*H*=CH_2), 3.14 (1H, d, J = 8.30, cis vinyl), 3.41 (1H, dd, J = 5.86, 6.35, C1—H), 3.51 (1H, d, J = 6.83, C4—H), 3.62 (1H, m, C5—H), 3.94 (1H, d, J = 12.7, trans vinyl), 5.01 (1H, dd, J = 5.62, 6.83, C3—H), 5.23 (1H, dd, J = 5.62, 5.86, C2-H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 9.60 (q, J = 129.1 Hz), 17.2 (q, J = 125.2), 22.7 (d, J = 129.1), 34.5 (d, J = 146.7), 43.2 (d, J = 168.3), 45.5 (t, J = 162.4), 47.3 (d, J = 172.2), 79.7 (d, J = 166.3), 80.4 (d, 172.2), 87.6 (d, J = 172.2), 96.5 (s).

[Cp*Ru(η^6-toluene)]OTf (**2b**): ^{1}H-NMR (270 MHz, $CDCl_3$, TMS) δ 1.98 (15H, s), 2.20 (3H, s), 5.70–5.77 (2H, m), 5.77–5.96 (m).

Reaction of (η^5-Pentamethylcyclopentadienyl)(η^4-isoprene)chlororuthenium(II) and Acetylene. The procedure for the reaction was similar to that described above. The reaction was performed using Cp*RuCl(isoprene) (**1c**; 17.4 mg, 0.0513 mmol), silver triflate (1.2 equiv), and acetylene (1 atm) in dichloromethane (7.5 mL) (3 h, −20 °C to room temperature). ^{1}H-NMR analysis indicated that **2a** and **2b** were formed 25.1 (0.0129 mmol) and 19.5% (0.0100 mmol) yields, respectively.

Reaction of (η^5-Pentamethylcyclopentadienyl)(η^4-1,3-butadiene)chlororuthenium(II) and 2-Butyne. The procedure for the reaction was similar to that described above. The reaction was performed using Cp*RuCl(butadiene) (**1a**; 100 mg, 0.307 mmol), silver triflate, and acetylene in dichloromethane (45 mL) (3 h, −20 °C to room temperature). The removal of solvent gave the pale yellow complex (**2c**; 143 mg, 94.2%).

[Cp*Ru(η^6-*o*-xylene)]OTf (**2c**): ^{1}H-NMR (270 MHz, $CDCl_3$, TMS) δ 1.92 (15H, s), 2.12 (6H, s), 5.70–5.78 (2H, m), 5.78–5.85 (2H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 10.2, 16.6, 87.2, 89.1, 95.2, 99.2. Anal. Calcd for $C_{19}H_{25}O_3SF_3Ru$: C, 46.43; H, 5.13. Found: C, 46.02; H, 5.09. MP: 128–130 °C dec.

Reactions of (η^5-Pentamethylcyclopentadienyl)(η^4-diene)chlororuthenium(II) and Deuterated Acetylene. The procedure for the reaction of Cp*RuCl(η^4-butadiene) and deuterated acetylene was similar to that described above, respectively.

(1) The reaction was performed using Cp*RuCl(η^4-butadiene) (**1a**; 16.2 mg, 0.0550 mmol), silver triflate, and C_2D_2 in dichloromethane (7 mL) (3 h, −70 °C to room temperature). The removal of solvent gave the pale yellow complex (24.3 mg). ^{1}H-NMR (500 MHz, $CDCl_3$, TMS): δ 0.69 (1H, m), 0.82 (0.64H, m), 1.86 (15H, s), 3.35 (1H, s), 3.41 (0.64H, m), 3.54 (0.66H, m), 3.62 (0.71H, m), 5.06–5.13 (1.48H, m) in **3a**; δ 2.03 (15H, s), 5.87 (1.47H, s) in **2a**. ^{2}D-NMR (41.3 MHz, $CDCl_3$): broad peaks appeared at 0.82, 3.03, 3.16, 3.41, 3.54, 3.62, 5.07, and 5.12 ppm corresponding to ^{1}H-NMR in **3a** and at the aromatic region in **2a**. ^{13}C{^{1}H}-NMR (67.8 MHz, $CDCl_3$): spectra analogous to those for **3a** and **2a** were observed except for a change of the 47.0 ppm signal (t, J_{C-D} = 23.4 Hz), and signals at 42.3 ppm and for the benzene ring were buried into the base line.

(2) The reaction was performed using Cp*RuCl(η^4-1,3-pentadiene) (**1b**; 20.7 mg, 0.0588 mmol), silver triflate and C_2D_2 in dichloromethane (7 mL) (3 h, −20 °C to room temperature). The removal of solvent gave the pale yellow complex (32.6 mg). ^{1}H-NMR (270 MHz, $CDCl_3$, TMS): δ 0.83 (3H, d, J = 7.32 Hz), 1.11–1.30 (1H, m), 1.84 (15H, s), 3.41 (0.46H, m), 3.51 (0.46H, m), 3.62 (0.42H, m), 3.94 (1H, s), 5.01 (1H, m), 5.23 (0.6H, m) in **3b**; δ 2.03 (15H, s), 5.87 (0.60H, s) in **2a**; δ 1.98 (15H, s), 2.20 (3H, s), 5.75–5.85 (3H, m) in **2b**. ^{2}D-NMR (41.3 MHz, $CDCl_3$): broad peaks appeared at 3.02, 3.14, 3.41, 3.51. 3.62, and 5.23 ppm corresponding to ^{1}H-NMR in **3b** and at the aromatic region in **2a** and **2b**. ^{13}C{^{1}H}-NMR (67.8 MHz, $CDCl_3$): spectra similar to those of **3a**, **2a**, and **2b** were observed except for the 45.5 ppm signal (t, J_{C-D} = 23.5 Hz), and signals at 43.2 and for the aromatic ring were buried into the base line.

(3) The reaction was performed using Cp*RuCl(η^4-isoprene) (**1c**; 16 mg, 0.0471 mmol), silver triflate, and C_2D_2 in dichloromethane (7 mL) (3 h, −20 °C room temperature). The removal of solvent gave the pale yellow complex (19.2 mg). ^{1}H-NMR (270 MHz, $CDCl_3$, TMS): δ 2.03 (15H, s) in **2a**; δ 1.98 (15H, s), 2.20 (3H, s), 5.75–5.85 (3H, m) in **2b**. ^{2}D-NMR (41.3 MHz, $CDCl_3$): broad peaks at the aromatic region in **2a** and **2b**. ^{13}C-{^{1}H}-NMR (67.8 MHz, $CDCl_3$): spectra similar to those of **2a** and **2b** were observed except for the disappearance of the aromatic ring signals.

Reaction of (η^5-Cyclopentadienyl)(η^4-1,3-butadiene)bromoruthenium(II) and Acetylene. Into a 30-mL round-bottom flask was placed the (diene)bromoruthenium complex (**1d**; 15 mg, 0.050 mmol) and acetone (10 mL). The flask was put in an acetone dry-ice bath kept at −30 °C. Acetylene gas (6.0 mL at 20 °C, 0.25 mmol) was added with stirring, followed by an acetone solution of silver triflate (0.1 N, 0.75 mL, 0.075 mmol). The acetone–dry-ice bath was gently warmed to room temperature for 3 h, and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was filtered through a Celite column. The filtrate was evaporated under reduced pressure. Recrystallization of the residue (dichloromethane/diethyl ether) gave the complex (**2d**; 18.8 mg, 95%) as pale ivory-white crystals.

[CpRu(η^6-benzene)]OTf (**2d**): ^{1}H-NMR (270 MHz, acetone-d_6) δ 5.55 (5H, s), 6.36 (6H, s); ^{13}C-NMR (67.8 MHz, acetone-d_6) δ 81.7, 87.6. Anal. Calcd for $C_{12}H_{11}O_3SF_3Ru$: C, 36.64; H, 2.82. Found: C, 36.42; H, 2.66. Mp: 205–207 °C dec.

Reaction of (η^5-Cyclopentadienyl)(η^4-isoprene)bromoruthenium(II) and Acetylene. The procedure for the reaction was similar to that described above. The reaction was performed from CpRuCl(isoprene) (**1e**; 15 mg, 0.050 mmol), silver triflate, and acetylene (5 equiv) in dichloromethane (10 mL) (7.5 h, −40 °C to room temperature). Removal of solvent gave the complex (**2e**; 53%).

[CpRu(η^6-benzene)]OTf (**2e**): ^{1}H-NMR (270 MHz, acetone-d_6) δ 2.37 (3H, s), 5.45 (5H, s), 6.17–6.33 (5H, m); ^{13}C-NMR (67.8 MHz, acetone-d_6) δ 21.1, 81.9, 88.2, 86.9, 88.7, 104.0.

Acknowledgment. The authors are indebted to Dr. A. Yanagisawa and Prof. H. Yamamoto of Nagoya University for measurements of the 500-MHz ^{1}H-NMR spectra. K.I. is grateful to the Ministry of Education, Science, and Culture, Japanese Government, for a Grant-in-Aid and to Mitsubishi Chemical Co. for financial support.

OM920795L