Skeletal Rearrangement of a C_2 Unit on a Triruthenium Cluster. Synthesis of μ-Ethylidene, μ_3-Ethylidyne, and μ_3-Vinylidene Complexes by the Reaction of $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ with Acetylene

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Reaction of the triruthenium pentahydride complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**; Cp* = η^5-C_5Me_5) with acetylene was investigated, in which the μ_3-ethylidene−μ_3-η^2(||)-ethyne complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}CMeH)\{\mu_3\text{-}\eta^2(||)\text{-}CH{=}CH\}$ (**2**) was produced via formation of the intermediary bis(μ-vinyl) complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)_2$ (**3**). An α-C−H bond of the μ-ethylidene ligand of **2** underwent oxidative addition upon thermolysis to yield the μ_3-ethylidyne−μ_3-η^2(||)-ethyne complex $(Cp^*Ru)_3(\mu\text{-}H)_2(\mu_3\text{-}CCH_3)\{\mu_3\text{-}\eta^2(||)\text{-}CH{=}CH\}$ (**5**), which showed fluxional behavior of both the μ_3-ethyne and the hydride ligands. Further C−H bond cleavage of the μ_3-ethylidyne ligand, affording the μ-vinylidene−μ_3-η^2(||)-ethyne complex $(Cp^*Ru)_3(\mu\text{-}H)(\mu_3\text{-}C{=}CH_2)\{\mu_3\text{-}\eta^2(||)\text{-}CH{=}CH\}$ (**6**), was also investigated. Treatment of **5** with an excess amount of acetylene resulted in C−C bond formation at the Ru_3 core, and the μ_3-ethylidyne−μ_3-η^3-diruthenaallyl complex $(Cp^*Ru)_3\{\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}C(H)C(H)CCH_3\}(\mu_3\text{-}CCH_3)$-($\mu$-H) (**7**) was obtained. The molecular structures of **5** and **7** were determined by single-crystal X-ray diffraction studies.

Introduction

A cluster complex has multiple metal centers in its structure. Since metal centers of the cluster can interact with a substrate cooperatively, it is anticipated that cluster complexes can activate substrates effectively.[1]

Although a large number of studies have been carried out so far on carbonyl clusters, little is known about the clusters that have no carbonyl ligands. It was well-known that a carbonyl ligand would reduce the electron density at the metal center, but an electron-rich metal center was desirable to activate inert molecules, such as an alkane and a dinitrogen. We have proved that the triruthenium pentahydride complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**), which has only pentamethylcyclopentadienyls as auxiliaries, was suitable for activating inert molecules in this regard.[2] Actually, C−H bond cleavage of an *n*-alkane has been achieved by **1**.[2f] Even a C−C bond of cyclopentadiene can undergo an oxidative addition reaction once it was incorporated into the Ru_3 reaction field.[2a]

Hydride ligands of complex **1** also play important roles for multimetallic activation, especially in the stage of generating a coordinatively unsaturated site on the cluster. When the substrate is coordinated to one ruthenium center, hydrides can be readily removed from the cluster as dihydrogen or by hydrogenation of an unsaturated molecule, such as alkenes. Especially, since reductive elimination took place between hydrides being in mutually cis positions, that is, between the doubly bridging hydride and the triply bridging hydride, this should result in simultaneous formation of coordinatively unsaturated sites on the same face of the Ru_3 plane (Scheme 1). Therefore, cooperative interaction among the substrate and the neighboring metal centers would be possible.

We have already reported the reactions of complex **1** with dienes,[2b] cyclic dienes,[2a,c] 1,1-disubstituted alkenes,[2h] and *n*-alkanes,[2f] in which formation of various hydrocarbyl ligands was observed. Some of these hydrocarbyl ligands underwent skeletal rearrangement reactions in a somewhat different manner from those of monometallic complexes; for example, regioselective C−C bond cleavage of 1,1-disubstituted alkenes[2h] and cleavage of one of the three Ru−Ru bonds to form a *closo*-ruthenacyclopentadiene complex.[2f,g] These skeletal rearrangement reactions would be caused by the cooperative interaction of the neighboring metal centers, but details of the reaction are still uncertain. It is important to prove the role of the neighboring metal centers to

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[1] See for example: (a) Adams, R. D.; Cotton, F. A. *Catalysis by Di- and Polynuclear Metal Cluster Complexes;* Wiley-VCH: Weinheim, Germany, 1998. (b) Dyson, P. J.; Mclndoe, J. S. *Transition Metal Carbonyl Cluster Chemistry*; Gordon and Breach Science: London, 2000.

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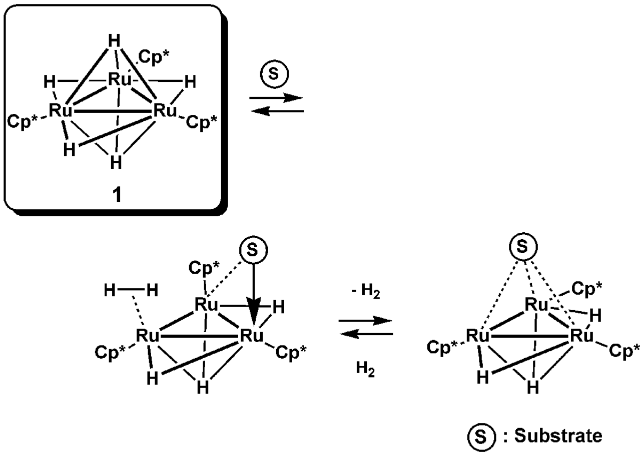
Scheme 1



appreciate *multimetallic activation*.[2,3] Because acetylene is the simplest and a reactive unsaturated C_2 hydrocarbon, it can serve as a probe for examining the basic reactivities of the cluster.

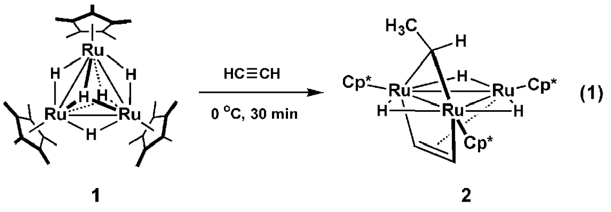
Many preceding studies using carbonyl clusters have been already carried out, and various coordination modes of an alkyne molecule on the cluster, such as μ-acetylide, μ-vinylidene, μ-ethylidene, μ_3-ethylidyne, etc. have been represented.[4] In contrast, little is known about the reactivities of non-carbonyl clusters toward alkynes, especially polyhydride clusters. One can expect a polyhydride cluster to clarify the stepwise rearrangement of a C_2 unit.

Puddephatt et al. have demonstrated insertion of an acetylene into the Pt−H bond of $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3]^+$, which finally resulted in the formation of a μ-vinylidene complex via cleavage of the α-C−H bond of the μ-vinyl intermediate.[5] Casey et al. also elucidated a detailed mechanism for the formation of a bis(μ_3-ethylidyne) complex by the reaction of $(Cp^*Co)_3H_4$ with acetylene.[6] It has been shown that there were two independent pathways to form an intermediary mono(μ_3-ethylidyne) complex (Scheme 2). A μ_3-η^2(||)-ethyne intermediate, which was formed by coordination of an acetylene followed by liberation of dihydrogen, was observed during the reaction. Insertion of the coordinated acetylene into one Co−H bond was confirmed by a labeling experiment using deuterated acetylene, which proved that a μ-ethylidene intermediate was formed by double insertion of the coordinated acetylene into the Co−H bonds.

We describe herein the reaction of **1** with acetylene and stepwise rearrangement of a C_2 unit on the Ru_3 plane together with a C−C bond formation to form a μ_3-allylic ligand.

Results and Discussion

Formation of the μ-Ethylidene−μ_3-η^2(||)-Ethyne Complex 2. Treatment of the triruthenium pentahydride complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**) with an excess amount of acetylene (1 atm) at 0 °C in THF resulted in an instant color change from purple to dark red. After 30 min, the solution turned orange. The μ-ethylidene−μ_3-η^2(||)-ethyne complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}CMeH)\{\mu_3\text{-}\eta^2\text{-}(||)\text{-}CH{=}CH\}$ (**2**) was isolated in 78% yield by the use of column chromatography on alumina (eq 1). Complex **1** reacted with two molecules of acetylene, and each acetylene was incorporated into each face of the Ru_3 core. This is in marked contrast to the reaction of **1** with 1 molar equiv of alkyne; the perpendicularly coordinated alkyne complexes $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2{:}\eta^2(\perp)\text{-}RCCR')$ are obtained by the reaction of **1** with terminal and internal alkynes.[7]



In the ^{1}H NMR spectrum of **2**, two signals assignable to the methyl groups of the Cp* ligands were observed at δ 1.68 and 1.79 with intensities of 30H and 15H, respectively. Two sharp signals for the three hydride ligands were observed at δ −18.27 and −16.98 in an intensity ratio of 2:1. They were still sharp even at −80 °C, and this shows that both the μ_3-η^2(||)-ethyne and the μ-ethylidene ligands of **2** were nonfluxional, at least on the NMR time scale. The fact that both resonances for the Cp* and the hydride were observed as two signals with an intensity ratio of 2:1 implies the C_s symmetrical structure of **2** with a mirror plane which bisects the Ru_3 triangle.

The signal of the hydrogen attached to the μ_3-η^2(||)-ethyne ligand appeared at δ 7.23 as a singlet. The ^{13}C signal of the μ_3-η^2(||)-ethyne ligand was observed at δ 136.8 (d, $J_{C-H} = 157$ Hz). These chemical shifts and the J_{C-H} value indicate the coordination of an acetylene in a μ_3-η^2(||) fashion.[8]

The ^{1}H signals of the α-hydrogen and the methyl group of the μ-ethylidene ligand were observed at δ 4.79 (dq, J = 6.7, 2.8 Hz) and δ 2.63 (d, J = 6.7 Hz), respectively. While the proton resonance of the α-hydrogen of a bridging alkylidene ligand was reported to appear between δ 5 and 11,[9] that of **2** was observed at significantly higher magnetic field. This upfield shift of the signal was most likely due to the shielding effect

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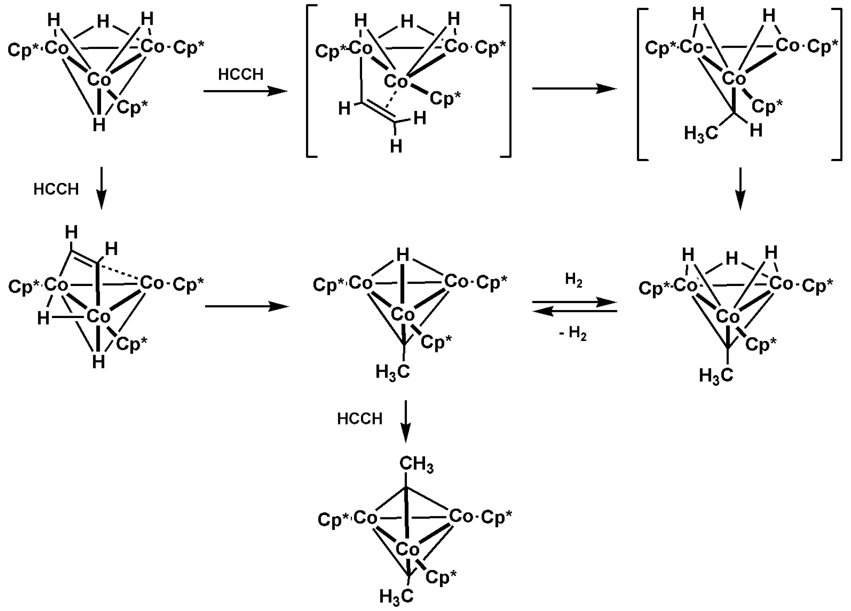
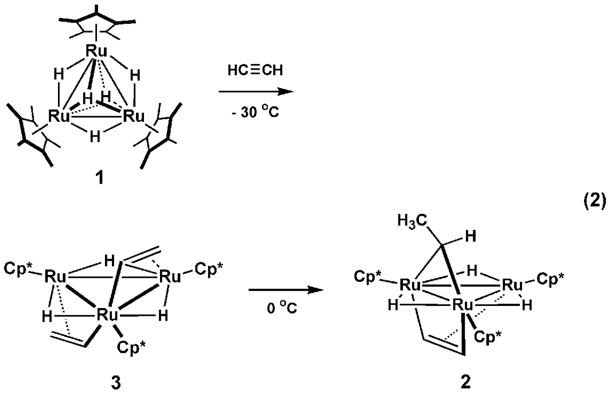
Scheme 2



by the three Cp* rings surrounding the μ-ethylidene ligand. The ^{13}C signal of the bridging carbon was observed at δ 128.3, which was also relatively higher than the reported values for the bridging alkylidene carbons (δ 100−210 ppm).[9] Although an agostic M−H−C interaction also leads to an upfield shift of the α-hydrogen and the bridging carbon,[10] such a M−H−C interaction should be ruled out on the basis of the J_{C-H} value (131 Hz) of the μ-alkylidene carbon, which lies in the normal range.[9]

Irradiation of the signal appeared at δ 4.79 caused a change in the line shape of the hydride signal observed at δ −16.89 from doublet to singlet, which indicates the presence of weak spin−spin coupling between the α-hydrogen and the hydride ligand.

When the reaction of **1** with an excess amount of acetylene was monitored by means of ^{1}H NMR spectroscopy at −30 °C, quantitative formation of the bis(μ-vinyl) complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}\eta^2\text{-}CH{=}CH_2)_2$ (**3**) was observed in the initial stage (eq 2). Although isolation



1

(2)

3

2

was disturbed by the thermal instability of **3**, the μ-η^1:η^2 coordination of the vinyl groups of **3** was unambiguously proved on the basis of the ^{1}H and the ^{13}C NMR data. The μ_3-η^2(||)-ethyne−μ-ethylidene complex **2** was then formed within 5 min at 0 °C with complete disappearance of **3**.

Treatment of complex **1** with 5 equiv of acetylene in THF-d_8 at −30 °C resulted in the formation of a 9:1 mixture of the bis(μ-vinyl) complex **3** and the μ_3-ethyne μ-ethylidene complex **2**. In the ^{1}H NMR spectra of this mixture, one set of signals assignable to a vinyl group was observed at δ 6.37 (dd, J = 9.4, 6.2 Hz), 3.68 (d, J = 9.4 Hz), and 2.36 (d, J = 6.2 Hz). The ^{13}C signals of the vinyl group appeared at δ 150.9 (d, J_{C-H} = 150.1 Hz) and 55.7 (dd, J_{C-H} = 163.1, 143.4 Hz). These data agreed well with the reported values for the analogous μ−σ,π-vinyl ligand in triosmium clusters.[8a,b,11]

Both the signals of the Cp* methyl groups and the hydride ligands were observed as a set of two signals with an intensity ratio of 2:1. This indicates that complex **3** belongs to a C_2 or C_s group. Four candidates for the structure of **3**, **A-1**, **A-2**, **B-1**, and **B-2**, are shown in Chart 1; while both vinyl groups are σ-bonded to one

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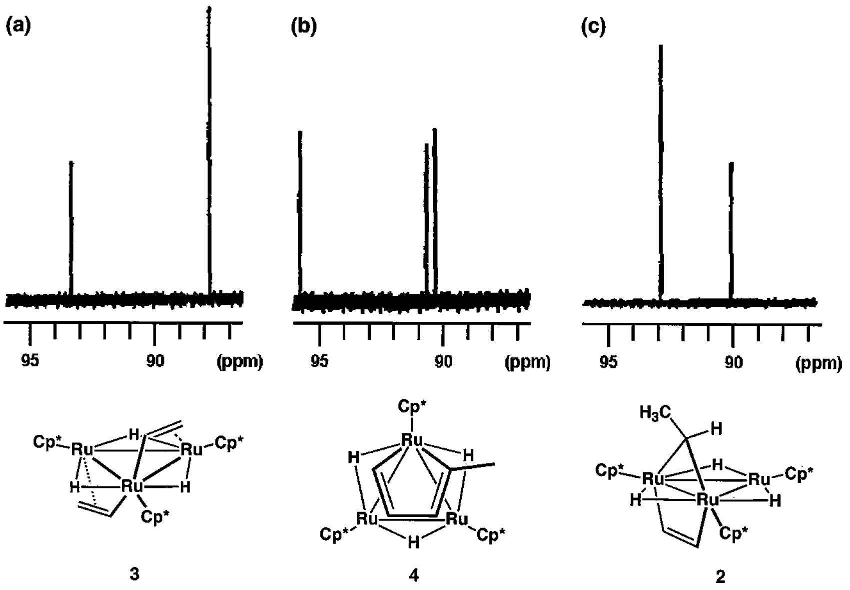
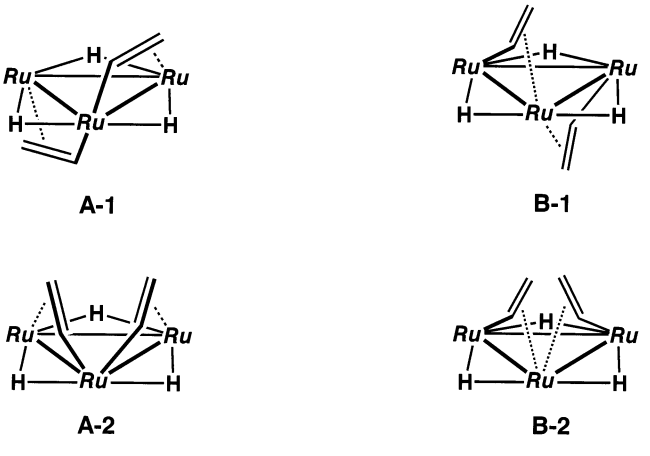


Figure 1. ^{13}C NMR spectra of the Cp* ring carbons of (a) $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}\eta^2\text{-}CH{=}CH_2)_2$ (**3**), (b) $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}CMe{=}CH{-}CH{=}CH)$ (**4**), and (c) $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}CMeH)\{\mu_3\text{-}\eta^2(\|)\text{-}CH{=}CH\}$ (**2**).

Chart 1



Ru = $(C_5Me_5)Ru$

ruthenium center in **A**, each vinyl group is σ-bonded to different ruthenium centers in **B**. Although it could not be determined whether two vinyl groups occupy the same side or different sides of the Ru_3 plane only on the basis of the NMR data, it can be assumed that two vinyl groups occupy the opposite side with respect to the Ru_3 plane by considering steric repulsion between the vinyl and the Cp* groups.

While formal oxidation states of the ruthenium centers of the type **A** structure were [Ru(II), Ru(II), Ru(IV)], those of type **B** were [Ru(III), Ru(III), Ru(II)]. Electron density at the metal center generally reflects the chemical shift of the Cp* ring carbons. When a carbon atom is σ-bonded to a metal center, it should reduce electron density at the metal center. Thus, the ^{13}C signal of the Cp* ring carbon attached to the metal center would appear at lower magnetic field because of the deshielding effect.

Actually, one of the Cp* ring signals of the *nido*-ruthenacyclopentadiene complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}CMe{=}CH{-}CH{=}CH)$ (**4**),[2a] which adopts formal [II–II–IV] ruthenium centers, appeared at a significantly lower region than the other two signals (Figure 1b). Complex **4** can be regarded as a model of the type **A** structure. In contrast, two of the Cp* ring signals of **2** appeared at lower magnetic field (Figure 1c). As mentioned above, formal oxidation states of the ruthenium centers of **2** are estimated at [IV–IV–II], which belongs to the type **B**.

In the ^{13}C NMR spectra of **3**, two signals with an intensity ratio of 1:2 were observed in the region of the Cp* ring carbon (Figure 1a; δ 94.9 and 88.0, respectively). The smaller signal appeared at lower magnetic field and the larger signal appeared at higher field. The pattern of the Cp* ring signals resembled that of **4**. Therefore, it was concluded that complex **3** adopted an **A-1** type structure, in which the two vinyl groups are σ-bonded to the same ruthenium center on the opposite face with regard to the Ru_3 plane.

Since the pentahydride complex **1** is a 44-electron complex, two additional acetylene molecules are possibly coordinated to **1** as a 2e donor according to the EAN rule. The reactivity of **1** with acetylene is distinct from that of the tricobalt tetrahydride complex $\{Cp^*Co(\mu\text{-}H)\}_3(\mu_3\text{-}H)$[6] (46e) because of the highly unsaturated character of **1**. As shown in Scheme 2, the reaction of $\{Cp^*Co(\mu\text{-}H)\}_3(\mu_3\text{-}H)$ with 2 molar equiv of acetylene proceeds stepwise to lead to a bis(μ_3-ethylidyne) complex via the intermediary mono(μ_3-ethylidyne) complex $\{Cp^*Co(\mu\text{-}H)\}_3(\mu_3\text{-}H)(\mu\text{-}CCH_3)$.

The bis(μ_3-η^2(||)-ethyne) complex $M_3(CO)_8(\mu_3\text{-}\eta^2(\|)\text{-}PhCCPh)_2$ (M = Fe, Ru, Os) has been obtained by thermal reaction of the mono(μ_3-η^2-ethyne) complex $M_3(CO)_{10}(\mu_3\text{-}\eta^2(\|)\text{-}PhCCPh)$ with alkyne.[12] After two carbonyl groups are eliminated, an alkyne is coordinated to the metal centers as a 4e donor. Although μ_3-η^2(||) coordination of two ethyne molecules is well-known, formation of **2** shows that insertion of an acetylene into an Ru–H bond of **1**, affording a μ-vinyl group, would be preferred to liberation of a dihydrogen, leading to μ_3-η^2(||) coordination of an acetylene. Insertion of a coordinated alkyne

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into an M−H bond to form a μ-vinyl ligand is well-known.[4a,8a,13]

Each vinyl group of **3** was then concomitantly transformed into the μ-ethylidene ligand and the μ_3-η^2(||)-ethyne ligand above and below the Ru$_3$ plane, respectively. Formation of a μ_3-η^2(||)-alkyne ligand on a cluster by way of β-C−H bond cleavage of a μ-vinyl group is also well-known.[4e,8a,13e,g,h]

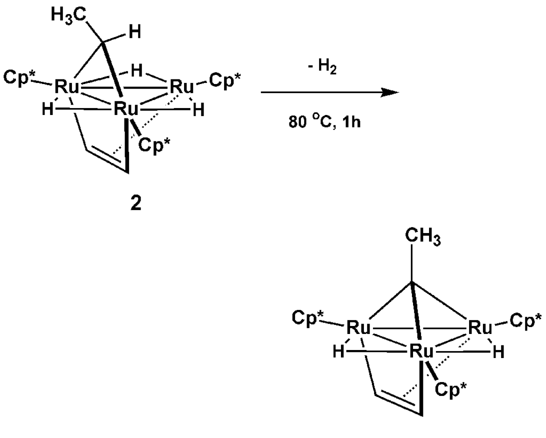
While numerous examples have been shown for the intermolecular nucleophilic attack of H$^-$ or PR$_3$ at the β-position of the μ-vinyl group to afford a μ-alkylidene complex by using an isolated cationic μ-vinyl complex,[14] only limited examples are known for the intramolecular nucleophilic attack of the hydride (insertion of a μ-vinyl group into an M−H bond).[13h,15] Lewis et al. have isolated a μ-alkylidene complex in the reaction of Os$_4$(CO)$_{11}$-(μ-H)$_3$(μ-η^2-HCCHPh) with CO at elevated temperature by way of insertion of a vinyl group into the Os−H bond.[13h]

Such a μ-alkylidene complex was often considered to be an intermediate of transformation of a coordinated alkyne to a μ_3-alkylidyne ligand. Casey proposed a μ-ethylidene intermediate during the formation of a μ-ethylidyne complex on the basis of the labeling experiment using C$_2$D$_2$.[6a]

As documented in the literature, each elementary step of the transformation of a μ-vinyl group into a μ_3-η^2(||)-ethyne and a μ-ethylidene ligand is plausible, as is formation of a μ-vinyl ligand via insertion of an acetylene into an M−H bond. Therefore, it can be considered that the μ-ethylidene μ_3-η^2(||)-ethyne complex **2**a is formed via the intermediary bis(μ-vinyl) complex **3**.

Formation of a μ_3-Ethylidyne−μ_3-η^2(||)-Ethyne Complex by Way of α-C−H Bond Cleavage of the μ-Ethylidene Ligand. Oxidative addition of an α-C−H bond of a μ-alkylidene ligand has been well documented in the literature, and sometimes an intermediary species with an α-agostic interaction was detected.[10] In these reactions, metal centers adjacent to the reaction site play a crucial role in the multimetallic activation. Thermolysis of the μ_3-ethylidene complex **2** was thus investigated.

Heating a solution of the μ-ethylidene−μ_3-η^2(||)-ethyne complex **2** at 80 °C resulted in the formation of the μ_3-ethylidyne−μ_3-η^2(||)-ethyne complex (Cp*Ru)$_3$(μ-H)$_2$(μ_3-η^2(||)-HC=CH)(μ_3-CCH$_3$) (**5**) (eq 3). Complex **5** was purified by the use of column chromatography on alumina and obtained in 88% yield. Complex **5** was fully characterized by means of the ^{1}H and ^{13}C NMR and IR spectroscopy and by elemental analysis.



(3)

In the ^{1}H NMR spectra of **5** measured at −35 °C, three singlets assignable to the methyl groups of the Cp* ligands were observed at δ 1.92, 1.82, and 1.78, respectively. Two signals of the hydride ligands were observed at δ −17.22 (dd, J = 4.0, 2.4 Hz) and δ −21.71 (d, J = 2.4 Hz) with the same intensity. The ^{1}H signals of the μ_3-ethyne ligand were also observed to be inequivalent at δ 8.61 (d, J = 2.8 Hz) and δ 6.11 (dd, J = 4.0, 2.8 Hz) at −35 °C. A spin-decoupling experiment revealed that one of the ethyne protons observed at δ 6.11 coupled with the hydride ligand observed at δ −17.22. All of these signals broaden and flatten at higher temperature (Figure 3). This implies that the site exchange between the two hydride ligands and the rotation of the μ_3-η^2(||)-ethyne ligand on the Ru$_3$ plane took place in complex **5**. We will discuss the fluxional process of **5** later.

The ^{13}C signals of the μ_3-η^2(||)-ethyne ligand of **5** were observed to be inequivalent at δ 118.2 (d, J_{C-H} = 156.0 Hz) and δ 156.4 (d, J_{C-H} = 150 Hz) at −35 °C. The ^{13}C signals of the μ_3-ethylidyne ligand appeared at δ 43.5 (q, J_{C-H} = 124.7 Hz) and δ 310.3 (s), respectively. These values are typical for a triply bridging ethylidyne group.

The structure of **5** was determined by X-ray crystallography using a red single crystal obtained from a cold toluene solution. The structure of **5**, shown in Figure 2, establishes the μ_3-η^2(||) coordination of acetylene and the μ_3-ethylidyne ligand, although locations of the hydride ligands were not determined. Crystal data for **5** are given in the Experimental Section (Table 3), and selected bond lengths and angles are listed in Table 1.

The Ru$_3$ core forms a nearly equilateral triangle with the sides being 2.73 Å. Each bond distance between the alkylidyne carbon, C(1), and ruthenium atoms lies within the range of a normal Ru−C σ-bond (Ru(1)−C(1) = 1.98(2) Å, Ru(2)−C(1) = 2.06(1) Å, Ru(3)−C(1) = 2.06(1) Å).

Since two carbon atoms of the μ_3-η^2(||)-ethyne ligand were disordered over the three positions, it is difficult

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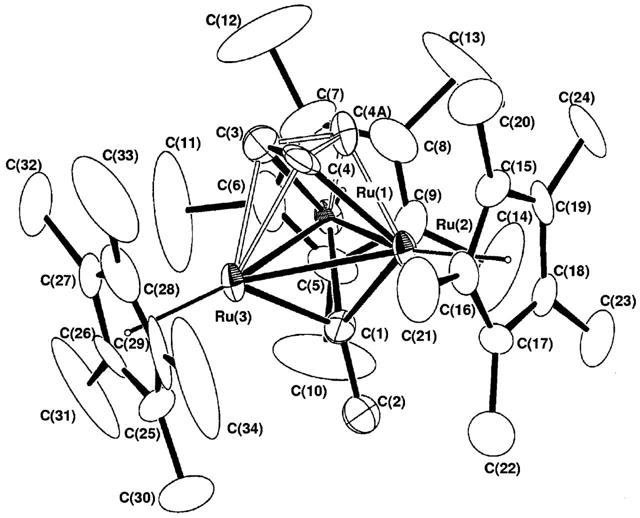


Figure 2. Molecular structure of $(Cp^*Ru)_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2(\|)\text{-}HC{=}CH)(\mu_3\text{-}CCH_3)$ (**5**), with thermal ellipsoids at the 30% probability level. The crystal submitted to the diffraction studies included a disordered form of **5** about the μ_3-η^2(||)-ethyne position, which is drawn in double lines. The two carbon atoms were disordered over the three positions C(3), C(4), and C(4A), with occupancies of 80, 60, and 60%, respectively.

to discuss bond lengths and angles precisely. However, this structure nicely exhibits the parallel coordination of the ethyne ligand to the Ru−Ru vector. The sum of the interior angles of the quadrangles Ru(1)−Ru(2)-C(4)−C(3) is 359°, which means that these four atoms are almost coplanar. The C(3)−C(4) distance of 1.30(3) Å lies in the range of the C−C bond length for the trimetallic μ_3-η^2(||)-HCCH complexes (1.26−1.41 Å).[8f,h−j,16]

A plausible reaction scheme from **2** to **5** is shown in Scheme 3. While path B involves α-C−H bond scission of the μ-ethylidene ligand, path A involves transformation of the μ_3-η^2(||)-ethyne ligand into a μ_3-ethylidyne ligand via formation of the μ_3-vinylidene intermediate as well as re-formation of a μ-vinyl group from the μ-ethylidene ligand.

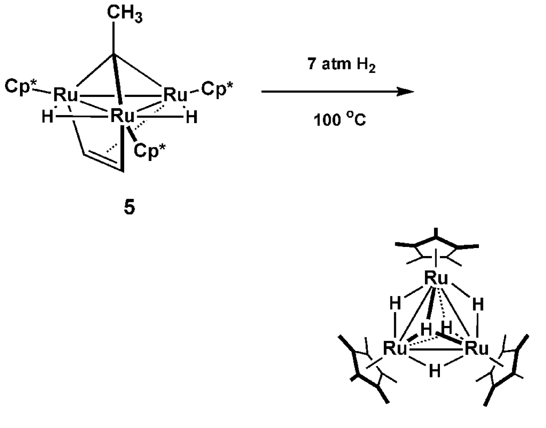
The μ_3-ethylidyne ligand was most likely formed by direct cleavage of the α-C−H bond of the μ-ethylidene ligand. The fact that no intermediate was detected during the reaction is quite consistent with path B. Besides, oxidative addition of an α-C−H bond of a μ-CH_2 group is well-known.[17]

In contrast to path B, path A involves transformation of both C_2 units above and below the Ru_3 face. Each elementary step has been well documented in the literature: for example, thermal transformation of a μ_3-η^2(||)-HCCR ligand into a μ_3-C=CHR ligand (step i of path A)[5,8b,14e,18] and conversion of the resultant μ-vinylidene intermediate to the corresponding μ_3-CCH_2R complex (step ii of path A).[11d,17c,19] Although it requires multistep transformation of the C_2 units, path A cannot be ruled out at this point.

Reaction of a μ_3-alkylidyne complex with hydrogen has been well investigated with regard to hydrogenation on the metal surface. In the sequence of the hydrogenation, transformation of a μ_3-methylidyne ligand into a μ-methylidene ligand was an important elementary step.

Bond formation between the triply bridging carbon and the hydride has been well elucidated.[20] Keister et al. have demonstrated reductive elimination between a μ_3-alkylidyne ligand and hydride ligands of $Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CX)$ (X = Ph, Cl, COOMe).[20b−d] The reactivity of the μ_3-alkylidyne carbon toward reductive bond formation is highly affected by the nature of the substituents X; when X = −COOMe, −SEt, stabilized μ-alkylidene and μ-alkyl complexes were obtained, respectively. Reductive elimination of the μ_3-alkylidyne ligand was also controlled by the nature of the metal center. While the μ_3-ethylidyne complex $M_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CMe)$ (M = Fe, Os) has been shown not to react with H_2,[8a,21] production of neohexane by the hydrogenation of $Ru_3(CO)_9(H)_3(\mu_3\text{-}CCH_2CMe_3)$ was reported.[22]

While the reaction of **5** with 1 atm of H_2 did not proceed even at 140 °C, quantitative formation of the pentahydride complex **1** was observed under pressurized H_2 conditions (eq 4; 7 atm of H_2, 100 °C).



5

1

Although the μ-ethylidene complex **2** has not been observed during hydrogenation of **5**, sequential C−H bond formation between the μ_3-ethylidyne carbon and

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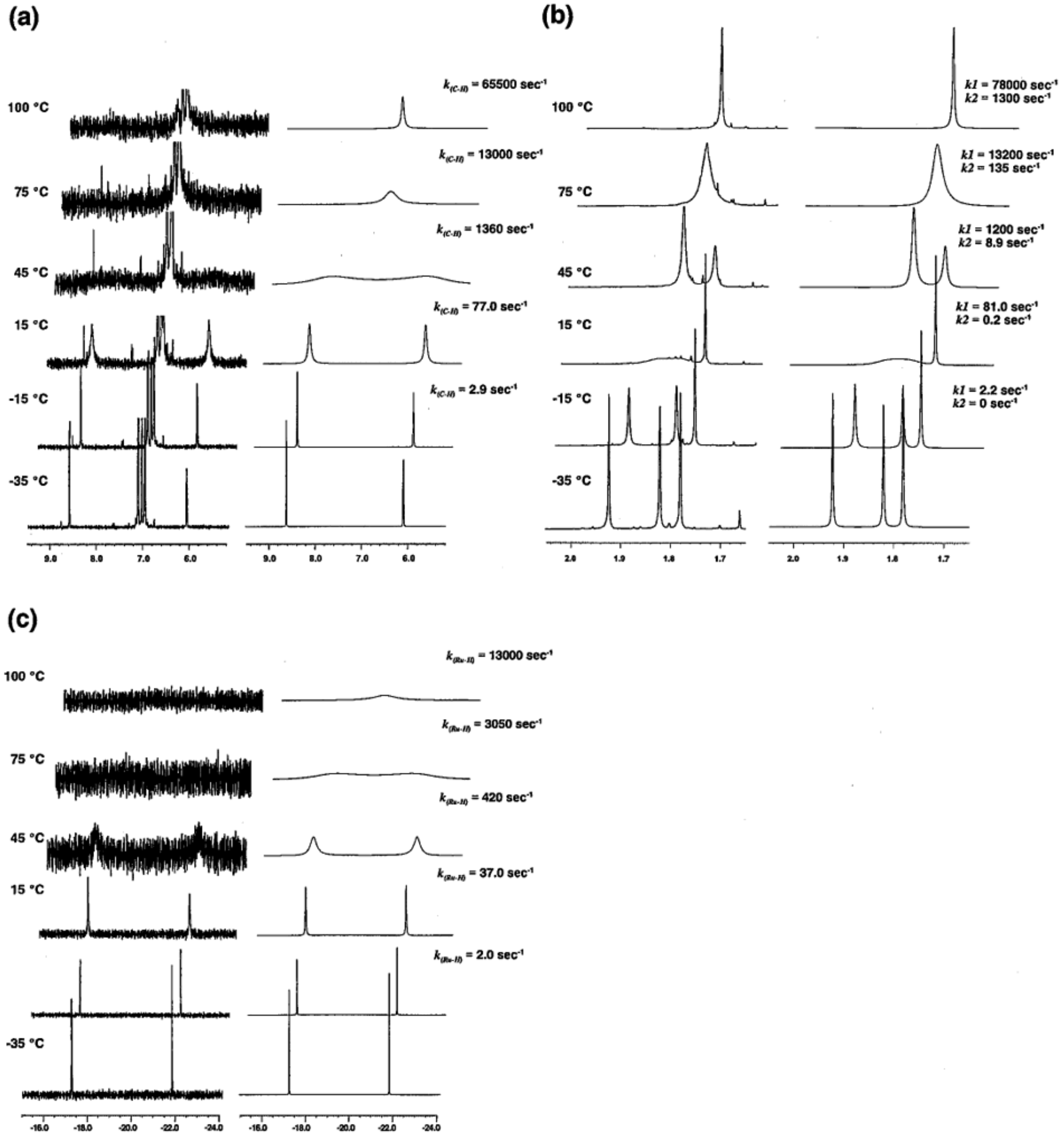


Figure 3. Variable-temperature ^{1}H NMR spectra of $(Cp^*Ru)_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2(||)\text{-}HC{=}CH)(\mu_3\text{-}CCH_3)$ (**5**) showing the regions for (a) the ethyne protons, (b) the Cp* methyl groups, and (c) the hydride protons together with the results of the simulation at right.

hydride ligands has to take place in **5**. The fates of the μ_3-η^2(||)-ethyne and the μ_3-ethylidyne ligands have still not been clarified, but they most likely were eliminated as ethane.

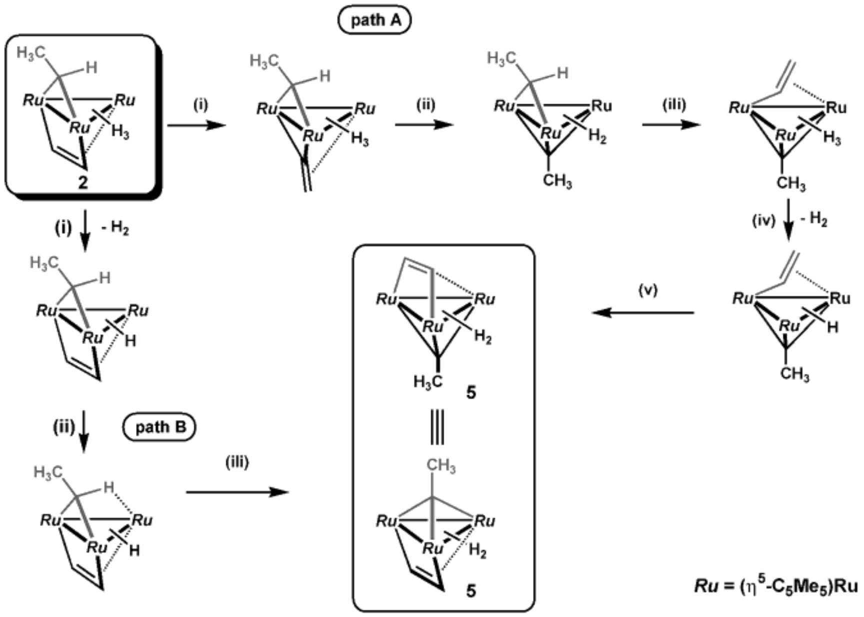
Fluxional Behavior of the μ_3-Ethylidyne−μ_3-η^2-(||)-Ethyne Complex 5. As mentioned above, the X-ray diffraction studies revealed that complex **5** has an unsymmetrical structure. The ^{1}H NMR spectrum measured at −35 °C was quite consistent with this structure. Signals for the ethyne, the Cp*, and the hydrides of **5**, however, broadened and flattened with elevating temperature. Figure 3 shows the changes in the line shape of the μ_3-η^2(||)-ethyne protons (Figure 3a), the Cp* signals (Figure 3b), and the hydrides (Figure 3c). Two of the three Cp* signals coalesced into one signal at 15 °C, and **5** began to show C_s symmetry. At this temperature, the Cp* signal observed at δ 1.78 was still sharp, but it began to broaden at 30 °C. All of the three Cp* signals coalesced into one signal at 65 °C. Above that temperature, the time-averaged C_3 folded axis was held in complex **5**. These results imply that **5** is fluxional within the NMR time scale. While only the site exchange of the hydride ligands took place at low temperature, the μ_3-η^2(||)-ethyne ligand began to move around the Ru_3 core at higher temperature.

Three processes, paths A−C, are proposed for the migration of the hydride ligands (Scheme 4). Path A requires only for H^b to move to the non-hydrogen-bridged Ru1−Ru3 bond. This generates a time-averaged plane of symmetry, and thereby it should result in coalescence of both of the ethyne signals, H^c and H^d, and the two Cp* signals, without the coalescence of

Table 1. Selected Bond Distances (Å) and Angles (deg) for 5

Ru(1)−Ru(2)	2.731(2)	Ru(1)−Ru(3)	2.727(2)	Ru(1)−C(1)	1.98(2)
Ru(1)−C(3)	2.16(2)	Ru(2)−Ru(3)	2.734(2)	Ru(2)−C(1)	2.06(1)
Ru(2)−C(4)	2.12(3)	Ru(3)−C(1)	2.06(1)	Ru(3)−C(3)	2.21(2)
Ru(3)−C(4)	2.22(2)	C(1)−C(2)	1.41(2)	C(3)−C(4)	1.30(3)
Ru(2)−Ru(1)−Ru(3)	60.13(5)	Ru(2)−Ru(1)−C(1)	48.7(4)	Ru(2)−Ru(1)−C(3)	71.2(5)
Ru(3)−Ru(1)−C(1)	48.9(4)	Ru(3)−Ru(1)−C(3)	52.2(5)	C(1)−Ru(1)−C(3)	95.8(7)
Ru(1)−Ru(2)−Ru(3)	59.86(5)	Ru(1)−Ru(2)−C(1)	46.1(4)	Ru(1)−Ru(2)−C(4)	69.7(4)
Ru(3)−Ru(2)−C(1)	48.5(4)	Ru(3)−Ru(2)−C(4)	52.7(6)	C(1)−Ru(2)−C(4)	94.1(8)
Ru(1)−Ru(3)−Ru(2)	60.02(5)	Ru(1)−Ru(3)−C(1)	46.2(5)	Ru(1)−Ru(3)−C(3)	50.5(5)
Ru(1)−Ru(3)−C(4)	68.6(8)	Ru(2)−Ru(3)−C(1)	48.4(4)	Ru(2)−Ru(3)−C(3)	70.5(5)
Ru(2)−Ru(3)−C(4)	49.4(8)	C(1)−Ru(3)−C(3)	91.8(7)	C(1)−Ru(3)−C(4)	91.1(9)
C(3)−Ru(3)−C(4)	34.2(8)	Ru(1)−C(1)−Ru(2)	85.2(5)	Ru(1)−C(1)−Ru(3)	84.9(5)
Ru(1)−C(1)−C(2)	133(1)	Ru(2)−C(1)−Ru(3)	83.1(5)	Ru(2)−C(1)−C(2)	125(1)
Ru(3)−C(1)−C(2)	128(1)	Ru(1)−C(3)−Ru(3)	77.3(6)	Ru(1)−C(3)−C(4)	106(1)
Ru(3)−C(3)−C(4)	73(1)	Ru(2)−C(4)−Ru(3)	77.9(9)	Ru(2)−C(4)−C(3)	112(2)
Ru(3)−C(4)−C(3)	72(1)				

Scheme 3



the signals of H^a and H^b. Path B involves direct site exchange between H^a and H^b, which results in coalescence of the hydride signals, and it does not affect the shape of both the Cp* and the ethyne signals. Path C involves stepwise migration via an intermediate with a symmetry plane, which bisects the ethyne ligand. Also, this process also results in coalescence between H^a and H^b together with H^c−H^d and two-Cp* exchange.

Activation parameters of the exchange for the two Cp* signals attached to Ru1 and Ru2 ($\Delta H^\ddagger = 16.9(2)$ kcal mol^{-1} and $\Delta S^\ddagger = 8.7(7)$ cal mol^{-1} K^{-1}), which were obtained by means of line-shape analysis, are quite consistent with those of the H^c−H^d exchange ($\Delta H^\ddagger = 16.5(1)$ kcal mol^{-1} and $\Delta S^\ddagger = 7.4(2)$ cal mol^{-1} K^{-1}). This means that these changes in the line shapes of the two Cp* signals and the ethyne protons arise from the same process. In contrast, activation parameters of the H^a−H^b exchange ($\Delta H^\ddagger = 14.0(1)$ kcal mol^{-1} and $\Delta S^\ddagger = -2.6(1)$ cal mol^{-1} K^{-1}) were remarkably different from those of the H^c−H^d and the two-Cp* exchange. If the hydrides moved around the Ru_3 core by way of path C, all of the exchange processes, H^a−H^b, H^c−H^d, and Cp*1−Cp*2, should show similar $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values. Therefore, it is concluded that the site exchange of the two Cp* and the ethyne protons arises from migration of the one hydride ligand (H^b) by way of path A.

As shown in Figure 3, the rate of the H^a−H^b exchange was smaller than the rate of H^b migration in path A. Consequently, if the site exchange between H^a and H^b proceeded by way of path C, it could not affect the line shapes of the Cp* and ethyne protons. Path B also does not cause the line shape change of the Cp* and the ethyne signals. Thus, it cannot be determined whether the fluxionality of the hydride signals arises from path B or path C. Both mechanisms, paths B and C, were proposed for the hydride exchange process of $H_2M_3(CO)_9$-(μ_3-η^2(||)-RCCR) (R = Os,[8e] Ru[23a]).

Such a hydride migration process has been often observed for a trimetallic complex containing two kinds

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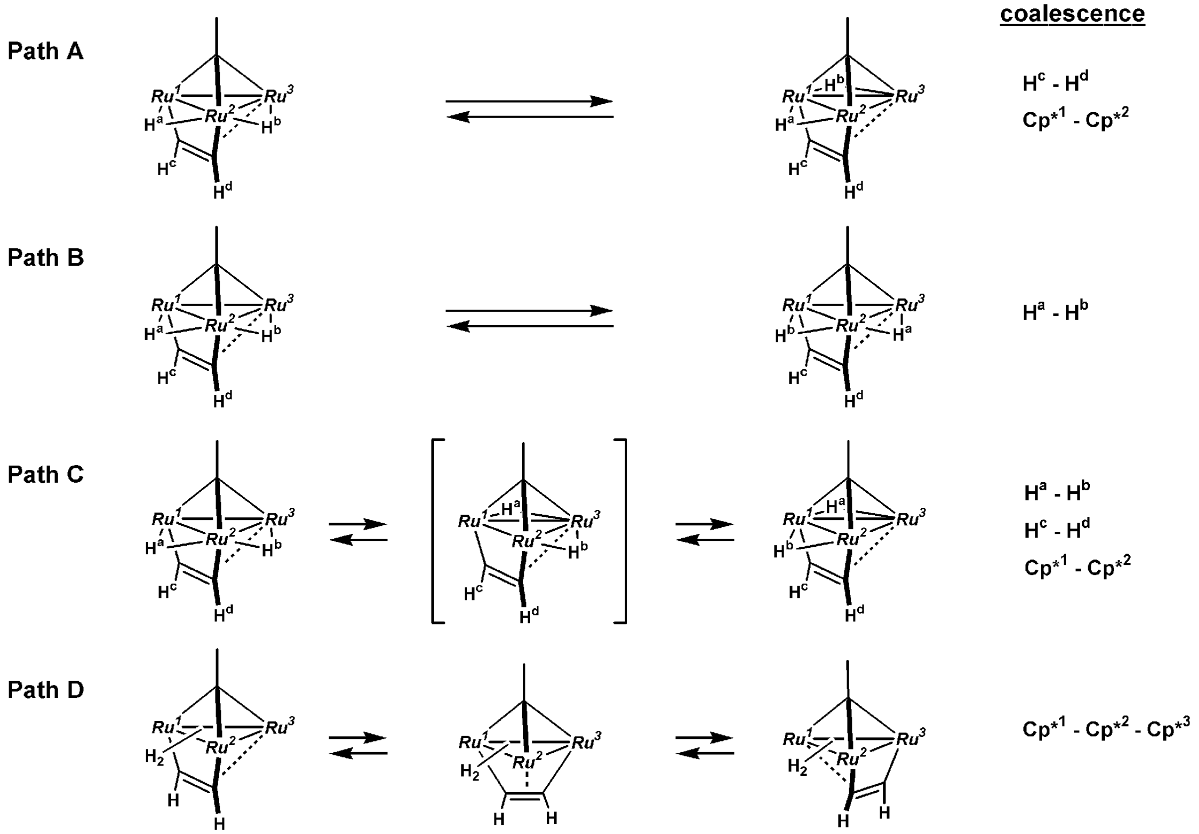
Scheme 4



of hydrides.[8e,23] A μ_3-alkylidene intermediate containing an agostic M−H−C interaction was often proposed for the site exchange of a hydride ligand of a μ_3-alkylidyne complex. Whereas there is no distinct evidence for an agostic intermediate of the fluxional process of **5**, the facts that **5** was formed by oxidative addition of a C−H bond of **2** and the reaction of **5** with H_2 afforded **1** imply reversible formation and cleavage of a C−H bond during the site exchange.

Above 65 °C, coalescence of all of the three Cp* signals was observed. This requires the μ_3-η^2(||)-ethyne ligand to migrate to all of the Ru−Ru bonds of **5**: i.e. successive pivot motions of the ethyne ligand (path D). Such motion of the coordinated alkyne has been commonly observed for trimetallic complexes having a μ_3-η^2(||)-alkyne ligand and has been well elucidated by Deeming et al.[5c,d,8d,g,13e,23a,b,d,24] Since the rate of the hydride exchange was much faster than the rotation of the μ_3-η^2(||)-ethyne ligand at any temperature, hydride ligands should be located equally on every Ru−Ru bond with regard to the ethyne ligand. Therefore, the successive pivot motions of the μ_3-η^2(||)-ethyne ligand would produce a time-averaged C_3 axis.

Activation parameters for path D were calculated at $\Delta H^\ddagger = 21.1(3)$ kcal mol^{-1} and $\Delta S^\ddagger = 11.7(8)$ cal mol^{-1} K^{-1}. The activation energy of path D at −10 °C was estimated at 18.0 kcal mol^{-1}, which was considerably higher than the reported values for the pivot motion of the triply coordinated alkynes. The activation energy of $H_2Ru_3(CO)_9(\mu_3$-η^2(||)-EtCCEt) was reported at 12.6 kcal mol^{-1} at −10 °C.[23a] Since both steric and electronic factors can affect the activation energy of the pivot motion, it is difficult to explain the difference. However, it has been shown that electron density at a metal center profoundly affects the activation energy for the pivot motion. For example, substitution of one of the carbonyl groups of $Os_3(CO)_{10}(\mu$-η^2(||)-EtCCEt) to PPh_3 resulted in an increase of the $\Delta G^\ddagger$ value for the pivot motion of the μ_3-η^2(||)-3-hexyne ligand from 14.5 to 16.3 kcal mol^{-1}.[24a] Thus, the high activation energy of the pivot motion of **5** seems to be caused by the strongly electron-donating Cp* ligands.

Thermolysis of a μ_3-Ethylidyne−μ_3-η^2(||)-Ethyne Complex To Yield a μ_3-η^2-Vinylidene−μ_3-η^2(||)-Ethyne Complex. Complex **5** was thermally labile and was converted to a μ_3-vinylidene complex upon heating. Thermolysis of the μ_3-ethylidyne−μ_3-η^2(||)-ethyne complex **5** at 180 °C in heptane quantitatively afforded the μ_3-η^2-vinylidene−μ_3-η^2(||)-ethyne complex $(Cp^*Ru)_3(\mu$-H)(μ_3-η^2(||)-HC=CH)(μ_3-C=CH$_2$) (**6**) by the β-C−H cleavage of the μ_3-ethylidyne ligand (eq 5). Transformation of a μ_3-alkylidyne ligand into a μ-vinylidene ligand on the cluster is well-known.[25] Complex **6** was fully characterized on the basis of the ^{1}H and ^{13}C NMR and IR spectra and by elemental analysis.

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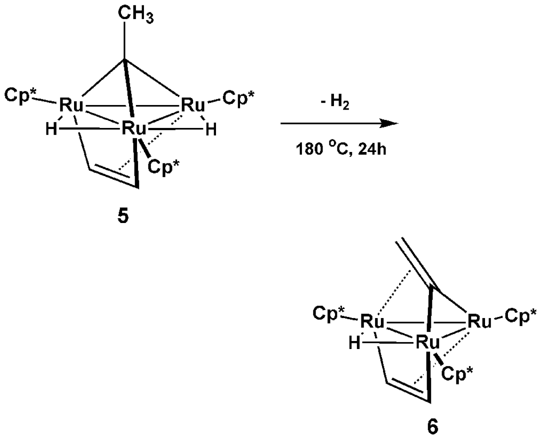


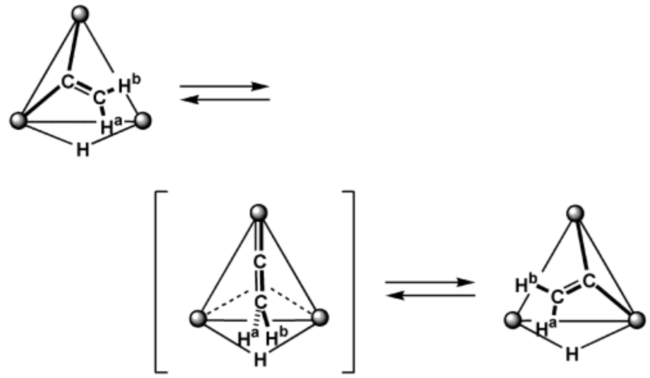
(5)

In the ^1H NMR spectra of **6** measured at 23 °C, three sharp signals which arose from the Cp* groups were observed at δ 1.88, 1.83, and 1.44, respectively. The methyne proton signals of the μ_3-η^2(||)-ethyne ligand were observed at δ 9.18 and 8.25 as doublets (J_{H-H} = 2.4 Hz). The ^{13}C signals of the μ_3-η^2(||)-ethyne ligand appeared at δ 151.5 (d, J_{C-H} = 151.0 Hz) and δ 148.7 (d, J_{C-H} = 156.9 Hz), respectively. These NMR data were quite consistent with those reported for the μ-η^2-(||)-HCCH structures.[8]

The vinylidene carbon signals were observed at δ 303.9 (s) and δ 70.1 (dd, J_{C-H} = 155.6, 154.9 Hz), which lie in the range of the reported values for trinuclear μ_3-vinylidene complexes.[4f,26] The vinylidene proton signals of **6** appeared at δ 4.79 and 3.62 with 1.2 Hz of spin−spin coupling between each other. Irradiation of the hydride signal observed at δ −27.41 (J_{H-H} = 1.2 Hz) resulted in a change in the coupling pattern of the vinylidene proton at δ 4.79, which showed that the hydride spin−spin coupled with only one vinylidene proton. Such asymmetrical spin−spin coupling between hydride and vinylidene protons suggests that the hydride ligand is not located between the ruthenium atoms that the vinylidene carbon was bridging.

There were several examples of μ_3-vinylidene complexes whose vinylidene protons were observed to be inequivalent. To the best of our knowledge, the difference in the chemical shifts of the vinylidene protons of the μ-C=CH^{a}H^b group, Δ(H^a−H^b), was less than 0.9 ppm.[8h,i,27] In contrast to the preceding μ-vinylidene complexes, that of **6** is considerably larger (Δ(H^a−H^b) = 1.17 ppm). Moreover, the chemical shift of δ 3.62 is relatively higher than those reported for the μ_3-vinylidene proton of the trimetallic system (δ 6.5−4.0).[26] This was probably due to the shield current effect of the surrounding Cp* ligands, and the signal which appeared at δ 3.62 was most likely assignable to the vinylidene proton H^b in Scheme 5, which is located opposite to the hydride ligand.

Scheme 5



While these NMR data indicate complex **6** adopts an unsymmetrical structure at low temperature, a time-averaged plane of C_s symmetry was formed in **6** at higher temperature. Two of the three Cp* signals and the two signals for the ethyne protons broadened and flattened as elevating temperature. In contrast, the signals for the vinylidene protons did not show any broadening (Figure 4). This means that the enantiomerization took place in **6**, and it brought about the time-averaged C_s plane (Scheme 5). Activation parameters for this fluxional process are estimated at $\Delta H^{\ddagger}$ = 14.1-(6) kcal mol^{-1} and $\Delta S^{\ddagger}$ = −14.2(18) cal mol^{-1} K^{-1} on the basis of the line-shape analysis of the Cp* signals. They are also calculated at $\Delta H^{\ddagger}$ = 14.5(7) kcal mol^{-1} and $\Delta S^{\ddagger}$ = −12.8(23) cal mol^{-1} K^{-1} from the ethyne signals. Such motion of the μ_3-vinylidene ligand has been well documented by Deeming et al. for $Os_3(\mu\text{-}H)_2\{\mu_3\text{-}C{=}C(OEt)H\}(CO)_9$, in which a large negative $\Delta S^{\ddagger}$ was also reported (ca. −24 cal mol^{-1} K^{-1}).[13e,28]

Since complex **6** has a time-averaged C_s plane in its structure at high temperature, the hydride ligand must be located on this C_s plane. Although it is also possible that the hydride is terminally coordinated to the ruthenium center on the C_s plane, we tentatively considered that the hydride ligand was located on the Ru−Ru edge that the μ_3-η^2(||)-ethyne was bridging, as shown in eq 5, on the basis of the lack of a sharp absorption due to ν(Ru−H) in the IR spectrum of **6**.

Formation of a μ_3-Diruthenaallyl−μ_3-Ethylidyne Complex by the Reaction of 5 with Acetylene. C−C bond formation on the cluster is important with regard to oligomerization and polymerization of unsaturated hydrocarbons on a metal surface. Heating a solution of **5** under 1 atm of acetylene led to the formation of the μ_3-ethylidyne−μ_3-η^3-diruthenaallyl complex $(Cp^*Ru)_3\{\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}C(H)C(H)CCH_3\}(\mu_3\text{-}CCH_3)(\mu\text{-}H)$ (**7**) (eq 6). Although there were several unidentified byproducts, complex **7** was isolated by means of column chromatography on alumina in 32% yield. Complex **7** was fully characterized on the basis of ^1H and the ^{13}C NMR and

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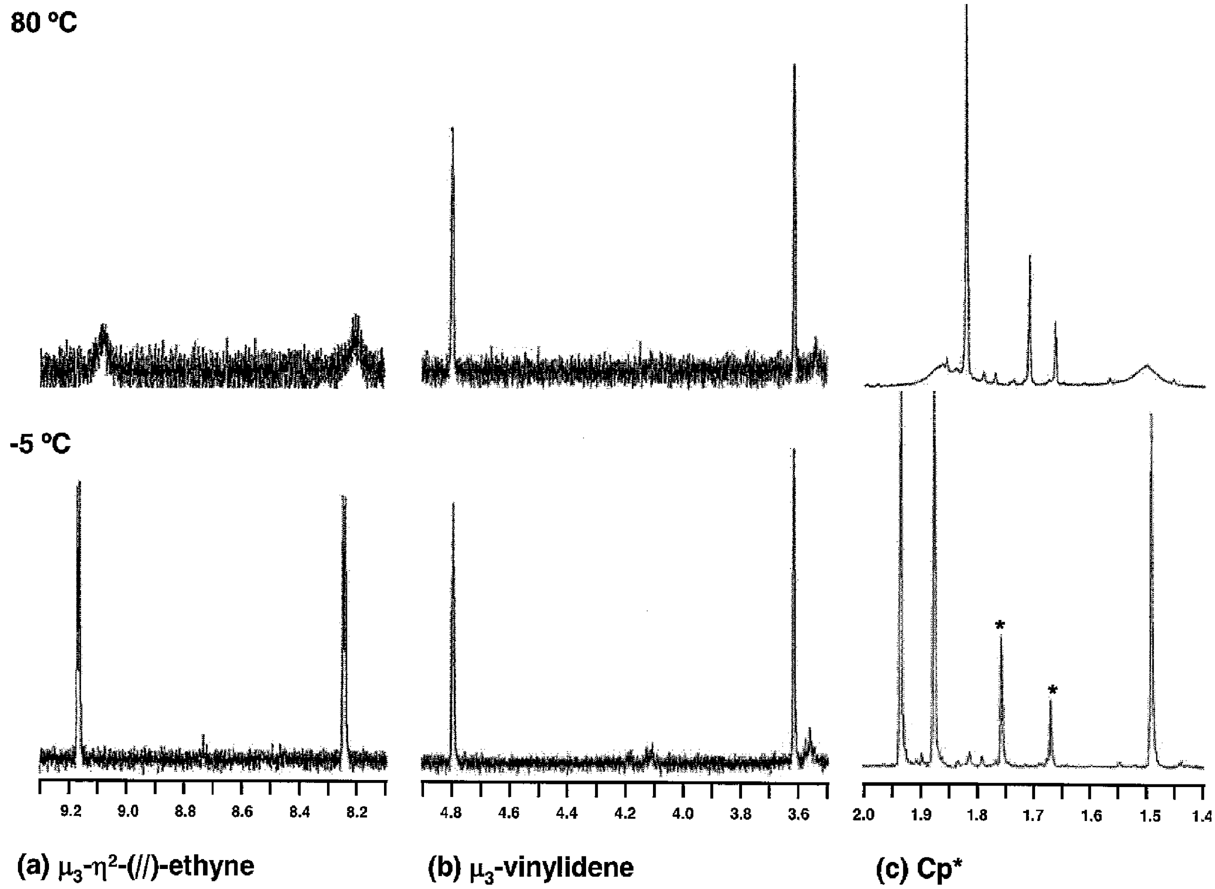
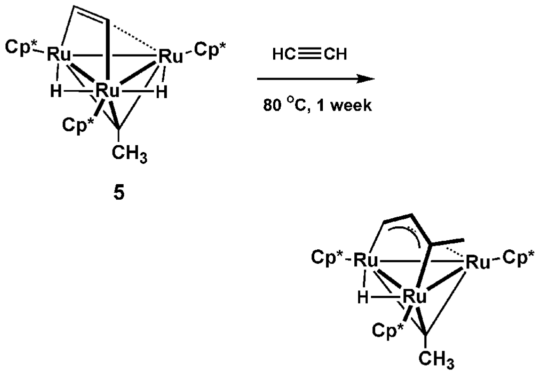
(28) Deeming et al. have not simulated fluxional behavior of the signals of $Os_3(\mu\text{-}H)_2\{\mu_3\text{-}C{=}C(OEt)H\}(CO)_9$, but they estimated $\Delta G^{\ddagger}$ at the different coalescence temperatures.[13e] While hydride signals coalesced at −18 °C, the CH_2 signals of the diastereotopic ethoxy group coalesced at −38 °C. The $\Delta S^{\ddagger}$ value, thus, can be estimated from $\Delta G^{\ddagger}_{Os-H}$ = 48 ± 2 kJ mol^{-1} (−18 ± 5 °C) and $\Delta G^{\ddagger}_{CH_2}$ = 46 ± 2 kJ mol^{-1} (−38 ± 5 °C).



(a) μ_3-η^2-(//)-ethyne (b) μ_3-vinylidene (c) Cp*

Figure 4. ^{1}H NMR spectrum of **6** measured at −5 °C (bottom) and 80 °C (top), showing the (a) μ_3-η^2(||)-ethyne, (b) μ_3-vinylidene, and (c) Cp* regions (400 MHz, toluene-d_8). Signals marked with an asterisk are derived from unidentified impurities.

IR data, and the structure of **7** was determined by an X-ray diffraction study.



5

7

(6)

In the ^{1}H NMR spectrum of **7**, three resonances for the Cp* groups appeared at δ 1.83, 1.77 and 1.45, respectively. The signals of the μ_3-1,3-diruthenaallyl moiety were observed at δ 8.57 (d, $J_{\mathrm{H-H}} = 5.6$ Hz, 1H), δ 5.19 (dd, $J_{\mathrm{H-H}} = 5.6$, 3.2 Hz, 1H), and δ 2.47 (s, 3H), which were assigned to the protons at the α- and β-positions of the diruthenacycle and methyl protons attached to the diruthenacycle, respectively. Spin−spin coupling between the proton attached to the central carbon and the hydride observed at δ −23.40 was observed to be $J_{\mathrm{H-H}} = 3.2$ Hz. Three ^{13}C signals assignable to the diruthenaallyl moiety were observed at δ 177.4 (d, $J_{\mathrm{C-H}} = 144.0$ Hz), δ 105.5 (d, $J_{\mathrm{C-H}} = 146.6$ Hz), and δ 177.4 (s) in the ^{13}C NMR spectra, respectively. These NMR data were quite consistent with those of the reported values for the trinuclear μ_3-η^1:η^3:η^1-dimetallaallyl complexes.[8a,29]

The X-ray diffraction studies of **7** were performed using a red single crystal obtained from a cold toluene solution. The structure of **7** is depicted in Figure 5. Although the hydride ligand could not be located, the μ_3-η^1:η^3:η^1 coordination of the C_3 moiety and the triply bridging ethylidyne ligand were clearly seen. The crystal data for **7** are given in Table 3, and selected bond lengths and bond angles are listed in Table 2.

The Ru−Ru bond lengths, 2.7943(6), 2.7450(7), and 2.7718(6) Å, correspond to an Ru−Ru single bond. The ethylidyne carbon, C(1), was disposed almost above the center of the Ru_3 triangle. Bond distances between the ruthenium atoms and C(1) were nearly equal: 1.981(4) Å for Ru(1)−C(1), 2.026(4) Å for Ru(2)−C(1), and 2.067(4) Å for Ru(3)−C(1). The Ru(1)−C(3) and Ru(2)−C(5) distances of 1.991(6) and 2.076(4) Å, respectively, are significantly shorter than those of Ru(3)−C(3), Ru(3)−C(4), and Ru(3)−C(5) (2.196(6), 2.193(6), and 2.156(4)

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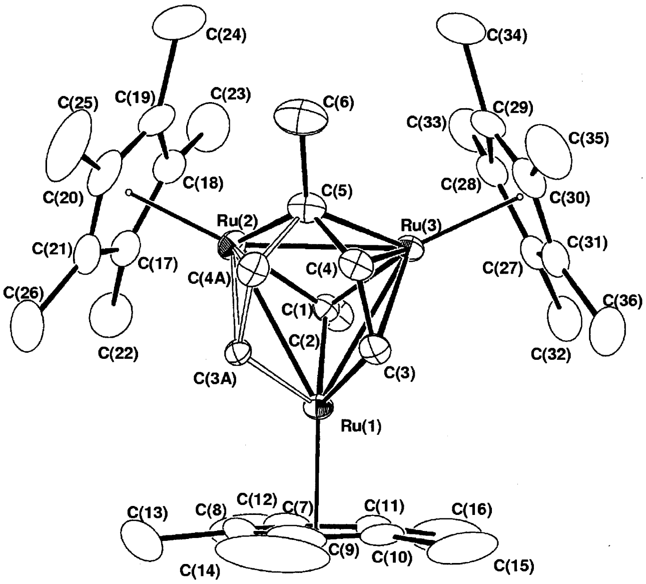

Figure 5. Molecular structure of $(Cp^*Ru)_3\{\mu_3\text{-}\eta^1:\eta^3:\eta^1\text{-}C(H)C(H)CCH_3\}(\mu_3\text{-}CCH_3)(\mu\text{-}H)$ (**7**), with thermal ellipsoids at the 30% probability level. The crystal submitted to the diffraction studies included a form of **7** disordered about the μ_3-η^1:η^3:η^1-allylic position in 31.7% amount which is shown by white lines.

Å, respectively), and they correspond to a Ru−C σ-bond. The latter were typical bond lengths for an Ru−C π-bond.

The sum of the bond angles around C(5) is 359.4°, which shows that the hybridization of C(5) is sp^2 rather than sp^3. The sum of the interior angles of the Ru_2C_3 moiety was 538.6°, which means that all of the five atoms forming the diruthenacyclopentadiene moiety, Ru(1), Ru(2), C(3), C(4), and C(5), are disposed almost on the same plane. The bond distances of 1.409(8) and 1.336(7) Å for C(3)−C(4) and C(4)−C(5), respectively, are within the range of those for a C−C double bond.

These bond lengths and angles indicate that the C_3 unit of **7** coordinates to Ru(1) and Ru(2) with two σ-bonds through C(3) and C(5) and three π-bonds to Ru(3): i.e., the μ_3-η^1:η^3:η^1-allylic coordination.

The formation of a μ_3-η^1:η^3:η^1-dimetallaallyl ligand by the reaction of the alkyne on the trimetallic cluster has been well documented in the literature.[29d−g,30] Several types of hydrocarbyls have been shown to undergo coupling reactions with alkynes. For example, Keister et al. proposed that a μ_3-η^3-allylic ligand was formed by insertion of a coordinated alkyne into an M−C bond of the μ_3-alkylidyne ligand.[30] Reductive elimination between a μ-η^2(||)-alkyne and a μ-methylidene, resulting in formation of a μ_3-η^3-dimetallaallyl complex on a triosmium cluster, has been also reported.[31] Knox et al. have elucidated insertion of an alkyne into an M−C bond of a μ-η^2(||)-alkyne ligand followed by C−C bond cleavage resulting in formation of a μ_3-alkylidyne μ_3-η^1:η^3:η^1-diruthenaallyl complex,[29d] which has a structure very similar to that of **7**.

It was not clear whether the C−C bond formation proceeded with the μ_3-η^2(||)-ethyne or the μ_3-ethylidyne ligand. Although the mechanism has not yet been elucidated, the coupling reaction of two molecules of acetylene was performed on the Ru_3 plane. This is regarded as a model reaction of oligomerization of alkynes at a metal surface. We are now investigating the reaction mechanism in detail using labeled acetylenes.

Conclusion

Sequential transformation of an acetylene molecule on the triruthenium cluster was observed by the reaction of $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**). At first, an acetylene inserts into an Ru−H bond to form a μ-η^1:η^2-vinyl ligand. Although the bis(μ-vinyl) complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}\eta^1:\eta^2\text{-}CH{=}CH_2)_2$ (**3**) could not be isolated, μ-σ,π-coordination of the vinyl group was confirmed by means of ^1H and ^{13}C NMR spectroscopy. The μ-ethylidene−μ_3-η^2(||)-ethyne complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}CMeH)\{\mu_3\text{-}\eta^2(||)\text{-}CH{=}CH\}$ (**2**) was then formed by way of cleavage of a β-C−H bond of the vinyl group and concomitant insertion of the vinyl group into an Ru−H bond at the opposite face of the Ru_3 plane. Oxidative addition of an α-C−H bond of the μ-ethylidene followed by liberation of dihydrogen afforded the μ_3-ethylidyne−μ_3-η^2(||)-ethyne complex $(Cp^*Ru)_3(\mu\text{-}H)_2(\mu\text{-}CMe)\{\mu_3\text{-}\eta^2(||)\text{-}CH{=}CH\}$ (**5**). Further C−H bond cleavage of the μ_3-ethylidyne afforded the μ_3-vinylidene μ_3-η^2(||)-ethyne complex $(Cp^*Ru)_3(\mu\text{-}H)(\mu_3\text{-}C{=}CH_2)\{\mu_3\text{-}\eta^2(||)\text{-}CH{=}CH\}$ (**6**). Although a detailed reaction mechanism is unclear at present, C−C bond formation was observed in the reaction of **5** with acetylene, which afforded the $\mu_3$ethylidyne−μ_3-η^3-diruthenaallyl complex $(Cp^*Ru)_3\{\mu_3\text{-}\eta^1:\eta^3:\eta^1\text{-}C(H)C(H)CCH_3\}(\mu_3\text{-}CCH_3)(\mu\text{-}H)$ (**7**). The reaction of **5** with dihydrogen regenerates **1** while liberating C_2 moieties from the Ru_3 plane.

A series of these reactions is a rare example of observing the sequential transformation of a C_2 unit from a μ-vinyl to a μ_3-vinylidene group on the cluster in each frame. Rearrangement of the C_2 unit proceeded as a consequence of the cooperative interaction of the multiple metal centers.

Reactions of the μ_3-ethylidyne μ_3-η^2(||)-ethyne complex **5** with dihydrogen and acetylene are regarded as model reactions for hydrogenation and oligomerization of acetylene on a metal surface, respectively. The reactivity of the coordinated hydrocarbon moieties on the Ru_3 cluster is now under investigation, aimed at proving the detailed mechanism for the formation of the vacant site on the cluster: i.e., the role of the hydride ligands.

Experimental Section

General Procedures. All experiments were carried out under an argon atmosphere. All compounds were treated with Schlenk techniques. Reagent grade toluene and THF were dried over sodium−benzophenone ketyl and stored under an argon atmosphere. Pentane was dried over phosphorus pentoxide and stored under an argon atmosphere. Benzene-d_6, toluene-d_8, and THF-d_8 were dried over sodium−benzophenone ketyl and stored under an argon atmosphere. Acetylene was used after being passed through concentrated H_2SO_4 and then a column packed with NaOH. IR spectra were recorded on JASCO FT/IR-5000 and Nicolet AVATAR 360 spectrophotometers. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-400 and Varian INOVA-400 Fourier transform spectrometers with tetramethylsilane as an internal standard. Variable-

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Table 2. Selected Bond Distances (Å) and Angles (deg) for 7

Ru(1)−Ru(2)	2.7943(6)	Ru(1)−Ru(3)	2.7718(6)	Ru(1)−C(1)	1.981(4)
Ru(1)−C(3)	1.991(6)	Ru(2)−Ru(3)	2.7450(7)	Ru(2)−C(1)	2.026(4)
Ru(2)−C(5)	2.076(4)	Ru(3)−C(1)	2.067(4)	Ru(3)−C(3)	2.196(6)
Ru(3)−C(4)	2.193(6)	Ru(3)−C(5)	2.156(3)	C(1)−C(2)	1.490(5)
C(3)−C(4)	1.409(8)	C(4)−C(5)	1.336(7)	C(5)−C(6)	1.519(6)

Ru(2)−Ru(1)−Ru(3)	59.09(2)	Ru(2)−Ru(1)−C(1)	46.5(1)	Ru(2)−Ru(1)−C(3)	83.7(2)
Ru(3)−Ru(1)−C(1)	48.1(1)	Ru(3)−Ru(1)−C(3)	51.8(2)	C(1)−Ru(1)−C(3)	98.8(2)
Ru(1)−Ru(2)−Ru(3)	60.04(2)	Ru(1)−Ru(2)−C(1)	45.1(1)	Ru(1)−Ru(2)−C(5)	84.6(1)
Ru(3)−Ru(2)−C(1)	48.5(4)	Ru(3)−Ru(2)−C(5)	50.8(1)	C(1)−Ru(2)−C(5)	98.1(2)
Ru(1)−Ru(3)−Ru(2)	60.86(1)	Ru(1)−Ru(3)−C(1)	45.5(1)	Ru(1)−Ru(3)−C(3)	45.4(2)
Ru(1)−Ru(3)−C(4)	74.8(2)	Ru(1)−Ru(3)−C(5)	83.8(1)	Ru(2)−Ru(3)−C(1)	47.3(1)
Ru(2)−Ru(3)−C(3)	81.4(2)	Ru(2)−Ru(3)−C(4)	74.5(2)	Ru(2)−Ru(3)−C(5)	48.3(1)
C(1)−Ru(3)−C(3)	90.0(2)	C(1)−Ru(3)−C(4)	108.9(2)	C(1)−Ru(3)−C(5)	94.4(2)
C(3)−Ru(3)−C(4)	37.5(2)	C(4)−Ru(3)−C(5)	35.8(2)	Ru(1)−C(1)−Ru(2)	88.4(1)
Ru(1)−C(1)−Ru(3)	86.4(1)	Ru(1)−C(1)−C(2)	126.6(3)	Ru(2)−C(1)−Ru(3)	84.2(1)
Ru(2)−C(1)−C(2)	129.1(3)	Ru(3)−C(1)−C(2)	127.7(3)	Ru(1)−C(3)−Ru(3)	82.8(2)
Ru(1)−C(3)−C(4)	126.6(5)	Ru(3)−C(3)−C(4)	71.2(3)	Ru(3)−C(4)−C(3)	71.4(3)
Ru(3)−C(4)−C(5)	70.6(3)	C(3)−C(4)−C(5)	120.7(5)	Ru(2)−C(5)−Ru(3)	80.8(1)
Ru(2)−C(5)−C(4)	123.0(4)	Ru(2)−C(5)−C(6)	123.6(4)	Ru(3)−C(5)−C(4)	73.6(3)
Ru(3)−C(5)−C(6)	124.6(3)	C(4)−C(5)−C(6)	112.8(5)		

temperature ^{1}H NMR spectra were recorded on a Varian INOVA-400 spectrometer. ^{2}H NMR spectra were recorded on a Bruker AM-400 spectrometer with benzene-d_6 as an internal standard. Field-desorption mass spectra were recorded on a Hitachi GC-MS M80 high-resolution mass spectrometer. Elemental analyses were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology.

X-ray Data Collection and Reduction. X-ray-quality crystals of **5** and **7** were obtained directly from the preparations described below and mounted on glass fibers. Diffraction experiments were performed on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) at 23 °C. Intensity data were collected using a $\omega/2\theta$ scan technique; 3 standard reflections were recorded every 150 reflections. The data for **5** and **7** were processed using the TEXSAN crystal solution package operating on an IRIS Indigo computer.[32] Neutral atom scattering factors were obtained from the standard sources.[33] In the reduction of the data, Lorentz/polarization corrections and empirical adsorption corrections based on azimuthal scans were applied to the data for each structure.

Structure Solution and Refinement for 5 and 7. The Ru atom positions were determined using direct methods employing the PATTY[34] direct-methods routines for **5** and **7**. In each case the remaining non-hydrogen atoms were located from successive difference Fourier map calculations using the DIRDIF-92 programs.[34] In both cases the non-hydrogen atoms were refined anisotropically by using full-matrix least-squares techniques on *F*. In the case of **5**, two carbon atoms of the μ_3-η^2(||)-HCCH ligand were disordered over the three sites C(3), C(4), and C(4A). Occupancies for each site were estimated at 80, 60, and 60%, respectively. In the case of **7**, two carbon atoms of the μ_3-η^1:η^3:η^1-C(H)C(H)CMe ligand, C(3) and C(4), were disordered over two sites related by C_s symmetry with 68.3 and 31.7% occupancy for each site. Crystal data and results of the analyses are listed in Table 3.

Table 3. Crystallographic Data for 5 and 7

	5	7
	(a) Crystal Parameters	
formula	$C_{34}H_{52}Ru_3$	$C_{36}H_{54}Ru_3$
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a, Å	16.306(6)	23.127(5)
b, Å	18.66(1)	22.840(5)
c, Å	11.109(8)	15.777(3)
α, deg		
β, deg	105.62(4)	127.31(1)
γ, deg		
V, Å^3	3254(5)	6628(2)
Z	4	8
D_{calcd}, g cm^{-1}	1.559	1.583
temp, °C	23	23
μ(Mo Kα), cm^{-1}	13.95	13.72
cryst dimens, mm	0.15 × 0.20 × 0.25	0.10 × 0.15 × 0.20
	(b) Data Collection	
diffractometer	Rigaku AFC-5R	
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)	
monochromator	graphite	
scan type	$\omega/2\theta$	
$2\theta_{max}$, deg	50.0	
scan speed, deg min^{-1}	16.0	
no. of rflns collected	6261	6160
no. of indep data	6244	6003
no. of indep data obsd	3639 ($I > 5.00\sigma(I)$)	4963 ($I > 3.00\sigma(I)$)
	(c) Refinement	
R	0.066	0.027
R_w	0.065	0.028
p factor	0.01	0.01
variables	343	371
GOF	3.65	3.00

Variable-Temperature NMR Spectra and Dynamic NMR Simulations. Variable-temperature NMR studies were performed in flame-sealed NMR tubes in toluene-d_8 for **5** using a Varian INOVA-400 Fourier transform spectrometer. NMR simulations for hydride ligands, ethyne protons, and Cp* signals of **5** were performed using gNMR v4.1.0 (1995−1999 Ivory Soft). Final simulated line shapes were obtained via an iterative parameter search upon the exchange constant *k*. Full details of the fitting procedure may be found in the Supporting Information. The rate constants that accurately modeled the experimental spectra at selected temperature are given in Figure 3. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined from the plot of ln(k/*T*) versus 1/*T*. Estimated standard deviations (σ) in the slope and *y* intercept of the Eyring plot determined the error in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively. The standard deviation in $\Delta G^{\ddagger}$ was determined from the formula $\sigma(\Delta G^{\ddagger})^2 = [\sigma(\Delta H^{\ddagger})]^2 + [T\sigma(\Delta S^{\ddagger})]^2 - 2T[\sigma(\Delta H^{\ddagger})][\sigma(\Delta S^{\ddagger})]$.

Preparation of $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}CMeH)\{\mu_3\text{-}\eta^2(||)\text{-}CH{=}CH\}$ (2). THF (20 mL) and $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}H)_2$ (**1**; 0.346 g, 0.485 mmol) were charged in a reaction flask (50 mL). The reaction flask was then degassed, and 1 atm of acetylene was subsequently introduced at −78 °C. The reaction mixture was gradually warmed to 0 °C and stirred for 30 min. The solution

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[32] TEXAN: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.

[33] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.

[34] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.

changed from reddish purple to orange. After the solvent was evaporated under reduced pressure, the orange residual solid was dissolved in 4 mL of toluene and purified by column chromatography on neutral alumina (Merck Art. No. 1097) with toluene. A 0.288 g amount of **2** was obtained as an orange solid on removal of the solvent under reduced pressure (78% yield). ^{1}H NMR (400 MHz, 23.0 °C, benzene-d_6): δ 7.51 (s, 2H, μ_3-*H*CCH), 4.94 (dq, J_{H-H} = 6.8, 2.7 Hz, 1H, μ-C*H*Me), 2.94 (d, J_{H-H} = 6.8 Hz, 3H, μ-CH*Me*), 1.92 (s, 15H, Cp*), 1.71 (s, 30H, Cp*), −16.82 (s, 1H, Ru*H*), −18.09 (s, 2H, Ru*H*). ^{13}C NMR (100 MHz, 23.0 °C, benzene-d_6): δ 136.4 (d, J_{C-H} = 154.5 Hz, μ_3-H*C*CH), 128.3 (d, J_{C-H} = 158.4 Hz, μ-*C*HMe), 93.8 (s, *C*$_5$Me$_5$), 89.0 (s, *C*$_5$Me$_5$), 41.4 (q, J_{C-H} = 123.3 Hz, μ-CH*Me*), 12.2 (q, J_{C-H} = 125.0 Hz, C$_5$*Me*$_5$), 10.4 (q, J_{C-H} = 125.0 Hz, C$_5$*Me*$_5$). IR (KBr, cm^{-1}): 2974, 2900, 1479, 1427, 1377, 1319, 1261, 1067, 1027, 777, 677. Anal. Calcd for $C_{34}H_{54}Ru_3$: C, 53.31; H, 7.11. Found: C, 52.72; H, 7.32.

Preparation of {Cp*Ru(μ-H)}$_3$(μ-η^2-CH═CH$_2$)$_2$ (3). THF-d_8 (0.5 mL) and {Cp*Ru(μ-H)}$_3$(μ-H)$_2$ (**1**; 16.2 mg, 22.7 μmol) were charged in an NMR tube capped with a natural rubber septum. Six equivalents of acetylene was added by the use of a gastight syringe at −78 °C. The solution was then warmed to −30 °C and stirred for 1 min. The ratio of **3** and **2**, measured by means of ^{1}H NMR spectroscopy, was 9:1. At this point, all of **1** was consumed. ^{1}H NMR (400 MHz, −30.0 °C, THF-d_8): δ 6.37 (dd, J_{H-H} = 9.4, 6.2 Hz, 2H, μ-C*H*═CHH′), 3.68 (d, J_{H-H} = 9.4 Hz, 2H, μ-CH═CH*H*′), 2.36 (d, J_{H-H} = 6.2 Hz, 2H, μ-CH═C*H*H′), 1.80 (s, 15H, Cp*), 1.63 (s, 30H, Cp*), −17.43 (s, 2H, Ru*H*), −25.35 (s, 1H, Ru*H*). ^{13}C NMR (100 MHz, −30.0 °C, THF-d_8): δ 150.9 (d, J_{C-H} = 150.1 Hz, μ-*C*H═CH$_2$), 94.9 (s, *C*$_5$Me$_5$), 88.0 (s, *C*$_5$Me$_5$), 55.7 (dd, J_{C-H} = 163.1, 143.4 Hz, μ-CH═*C*H$_2$), 11.4 (q, J_{C-H} = 125.0 Hz, C$_5$*Me*$_5$), 10.7 (q, J_{C-H} = 125.9 Hz, C$_5$*Me*$_5$).

Preparation of (Cp*Ru)$_3$(μ-H)$_2$(μ_3-η^2(||)-HC═CH)(μ_3-CCH$_3$) (5). Toluene (15 mL) and {Cp*Ru(μ-H)}$_3$(μ-CMeH){μ_3-η^2(||)-CH═CH} (**2**; 0.288 g, 0.376 mmol) were charged in a reaction flask. The reaction flask was heated at 80 °C for 1 h. After the solvent was evaporated under reduced pressure, the residual solid was dissolved in 3 mL of toluene and the solution was purified by column chromatography on neutral alumina (Merck Art. No. 1097) with toluene. A 0.252 g amount of **5** was obtained as a dark yellow solid on removal of the solvent under reduced pressure (88% yield). A single crystal of **5** was obtained from toluene solution at −20 °C. ^{1}H NMR (400 MHz, 23.0 °C, benzene-d_6): δ 8.60 (dd, 1H, μ_3-*H*CCH), 6.09 (br s, 1H, μ_3-HCC*H*), 3.39 (s, 3H, μ_3-C*Me*), 1.85 (br s, 30H, Cp*), 1.77 (s, 15H, Cp*), −17.19 (br s, 1H, Ru*H*), −21.81 (s, 1H, Ru*H*). ^{1}H NMR (400 MHz, −35.0 °C, toluene-d_8): δ 8.62 (dd, J_{H-H} = 4.0, 2.9 Hz, 1H, μ_3-*H*CCH), 6.11 (d, J_{H-H} = 2.9 Hz, 1H, μ_3-HCC*H*), 3.39 (s, 3H, μ_3-C*Me*), 1.92 (s, 15H, Cp*), 1.82 (s, 15H, Cp*), 1.78 (s, 15H, Cp*), −17.19 (dd, J_{H-H} = 4.0, 2.9 Hz, 1H, Ru*H*), −21.81 (d, J_{H-H} = 2.9 Hz 1H, Ru*H*). ^{13}C NMR (100 MHz, 23.0 °C, benzene-d_6): δ 310.3 (s, μ_3-*C*Me), 156.5 (br, μ_3-H*C*CH), 118.9 (br, μ_3-HC*C*H), 94.3 (s, *C*$_5$Me$_5$), 93.9 (s, *C*$_5$Me$_5$), 43.5 (q, J_{C-H} = 124.7 Hz, μ-C*Me*), 11.5 (q, J_{C-H} = 125.3 Hz, C$_5$*Me*$_5$), 11.3 (q, J_{C-H} = 126.6 Hz, C$_5$*Me*$_5$). IR (KBr, cm^{-1}): 2974, 2908, 1808, 1671, 1479, 1290, 1168, 1029, 1000, 790, 661. Anal. Calcd for $C_{34}H_{52}Ru_3$: C, 53.45; H, 6.86. Found: C, 53.31; H, 6.60.

Reaction of (Cp*Ru)$_3$(μ-H)$_2$(μ_3-η^2(||)-HC═CH)(μ_3-CCH$_3$) (5) with 7 atm of H$_2$. Toluene (10 mL) and (Cp*Ru)$_3$(μ-H)$_2$-(μ_3-η^2(||)-HC═CH)(μ_3-CCH$_3$) (**5**; 32.0 mg, 0.042 mmol) were charged in a 50 mL glass autoclave. After the reaction vessel was degassed, 7 atm of H$_2$ was introduced. The reaction vessel was heated at 100 °C for 50 h. The solvent was then evaporated under reduced pressure, and 30.0 mg of dark reddish residual solid was obtained. Exclusive formation of the triruthenium pentahydride complex {Cp*Ru(μ-H)}$_3$(μ_3-H)$_2$ (**1**) was confirmed by means of ^{1}H NMR spectroscopy.

Reaction of (Cp*Ru)$_3$(μ-H)$_2$(μ_3-η^2(||)-HC═CH)(μ_3-CCH$_3$) (5) with 1 atm of H$_2$. An NMR tube equipped with a Roto Tite valve was charged with benzene-d_6 (0.4 mL) and (Cp*Ru)$_3$(μ-H)$_2$(μ_3-η^2(||)-HC═CH)(μ_3-CCH$_3$) (**5**; 5.0 mg, 6.5 μmol). The tube was degassed and then charged with 1 atm of hydrogen. The tube was then heated at 140 °C for 24 h. During the reaction, no detectable products were observed except for ^{1}H signals for **5**.

Preparation of (Cp*Ru)$_3$(μ-H)(μ_3-η^2(||)-HC═CH)(μ_3-C═CH$_2$) (6). Heptane (5 mL) and (Cp*Ru)$_3$(μ-H)$_2$(μ_3-η^2(||)-HC═CH)(μ_3-CCH$_3$) (**5**; 41.7 mg, 0.0546 mmol) were charged in a glass autoclave. The reaction flask was heated at 180 °C for 24 h. After the solvent was evaporated under reduced pressure, the residual solid was dissolved in 3 mL of toluene and the solution was purified by column chromatography on neutral alumina (Merck Art. No. 1097) with toluene. A 37.0 mg amount of **6** was obtained as a red solid on removal of the solvent under reduced pressure (91% yield). ^{1}H NMR (400 MHz, 23.0 °C, benzene-d_6): δ 9.18 (d, J_{H-H} = 2.4 Hz, μ_3-*H*CCH), 8.25 (d, J_{H-H} = 2.4 Hz, μ_3-HCC*H*), 4.79 (dd, J_{H-H} = 1.2, 1.2 Hz, 1H, μ_3-C═C*H*$_2$), 3.62 (d, J_{H-H} = 1.2 Hz, 1H, μ_3-C═C*H*$_2$), 1.88 (s, 15H, Cp*), 1.83 (s, 15H, Cp*), 1.44 (s, 15H, Cp*), −27.41 (s, 1H, Ru*H*). ^{13}C NMR (100 MHz, 23.0 °C, benzene-d_6): δ 303.9 (s, μ_3-*C*═CH$_2$), 151.5 (d, J_{C-H} = 151.0 Hz, μ_3-H*C*CH), 148.7 (d, J_{C-H} = 156.9 Hz, μ_3-HC*C*H), 93.3 (s, *C*$_5$Me$_5$), 92.0 (s, *C*$_5$Me$_5$), 91.5 (s, *C*$_5$Me$_5$), 70.1 (dd, J_{C-H} = 155.6, 154.9 Hz, μ_3-C═*C*H$_2$), 12.0 (q, J_{C-H} = 125.5 Hz, C$_5$*Me*$_5$), 11.9 (q, J_{C-H} = 125.5 Hz, C$_5$*Me*$_5$), 10.7 (q, J_{C-H} = 125.5 Hz, C$_5$*Me*$_5$). IR (KBr, cm^{-1}): 2974, 2894, 2851, 1475, 1442, 1371, 1316, 1280, 1154, 1069, 1025. Anal. Calcd for $C_{34}H_{52}Ru_3$: C, 53.59; H, 6.61. Found: C, 53.47; H, 6.61.

Preparation of (Cp*Ru)$_3${μ_3-η^1:η^3:η^1-C(H)C(H)CCH$_3$}(μ_3-CCH$_3$)(μ-H) (7). Toluene (15 mL) and {Cp*Ru(μ-H)}$_3$(μ-H)$_2$ (**1**; 0.131 g, 0.184 mmol) were charged in a reaction flask (50 mL). The reaction flask was then degassed, and 1 atm of acetylene was subsequently introduced at −78 °C. After the reaction flask was gradually warmed to room temperature, the solution was heated at 80 °C for 7 days with vigorous stirring. The solution turned from orange to red with formation of a black precipitate, which was sparingly soluble in organic solvents and readily separated by filtration. The filtrate was then evaporated under reduced pressure. The residual solid was dissolved in 3 mL of toluene and the solution purified by column chromatography on neutral alumina (Merck Art. No. 1097) with toluene. A 0.047 g amount of **7** was obtained as a dark red solid on removal of the solvent under reduced pressure (88% yield). A single crystal of **7** was obtained from toluene solution at −20 °C. ^{1}H NMR (400 MHz, 23.0 °C, benzene-d_6): δ 8.57 (d, J_{H-H} = 5.4 Hz, 1H, μ_3-C(*H*)C(H)CMe), 5.19 (dd, J_{H-H} = 5.4, 3.2 Hz, 1H, μ_3-C(H)C(*H*)CMe), 4.16 (s, 1H, μ_3-C*Me*), 2.47 (s, 3H, μ_3-C(H)C(H)C*Me*), 1.83 (s, 15H, Cp*), 1.77 (s, 15H, Cp*), 1.45 (s, 15H, Cp*), −23.40 (d, J_{H-H} = 3.2 Hz, 1H, Ru*H*). ^{13}C NMR (100 MHz, 23.0 °C, benzene-d_6): δ 332.0 (s, μ_3-*C*Me), 182.2 (s, μ_3-HCC(H)*C*Me), 177.4 (d, J_{C-H} = 144.0 Hz, μ_3-*C*(H)C(H)CMe), 105.1 (d, J_{C-H} = 146.1 Hz, μ_3-C(H)*C*(H)CMe), 94.7 (s, *C*$_5$Me$_5$), 94.2 (s, *C*$_5$Me$_5$), 91.4 (s, *C*$_5$Me$_5$), 46.4 (q, J_{C-H} = 124.0 Hz, μ_3-C*Me*), 36.1 (q, J_{C-H} = 122.9 Hz, μ_3-C(H)C(H)C*Me*), 11.5 (q, J_{C-H} = 125.4 Hz, C$_5$*Me*$_5$), 10.2 (q, J_{C-H} = 125.5 Hz, C$_5$*Me*$_5$). IR (KBr, cm^{-1}): 2944, 2900, 1479, 1429, 1375, 1294, 1230, 1169, 1023, 1007, 990, 862, 735. Anal. Calcd for $C_{36}H_{54}Ru_3$: C, 54.73; H, 6.89. Found: C, 54.84; H, 7.04.

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Supporting Information Available: X-ray crystallographic files of **5** and **7** in CIF form and tables and figures giving parameters and results for the dynamic NMR studies of **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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