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Synthesis, structure, and property of a triruthenium cluster having a μ-alkyl ligand: Transformation of a $\mu_3(\perp)$-alkyne ligand into a μ-alkyl ligand via a μ_3-vinylidene complex

Ryu-ichi Tenjimbayashi, Eisuke Murotani, Toshifumi Takemori, Toshiro Takao, Hiroharu Suzuki *

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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Abstract

A triruthenium μ-alkyl complex, $(Cp^*Ru)_3(\mu\text{-}\eta^2\text{-}HCHCH_2R)(\mu\text{-}CO)_2(\mu_3\text{-}CO)$ (**2a**, R = Ph; **2b**, R = ^{t}Bu, $Cp^* = \eta^5\text{-}C_5Me_5$), which contains a two-electron and three-center interaction among Ru, C, and H atoms, has been synthesized by the reaction of a perpendicularly coordinated 1-alkyne complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}RCCH)$ (**1a**; R = Ph, **1b**; R = ^{t}Bu), with carbon monoxide. A diffraction study for **2b** clearly represented the bridging neohexyl group on one Ru–Ru edge. This μ-alkyl group exhibited dynamic behavior resulting in site-exchange of the α-hydrogen atoms between the terminal and bridging positions, which was synchronized with the migration of the μ-alkyl groups between the two ruthenium atoms. The agostic C–H bond was readily cleaved upon pyrolysis. Whereas the μ-phenethylidene intermediate resulting from the σ-C–H bond cleavage has never been observed, a μ_3-phenethylidyne complex, $\{Cp^*Ru(\mu\text{-}CO)\}_3(\mu_3\text{-}CCH_2Ph)$ (**7a**), and a μ_3-methylidyne complex, $\{Cp^*Ru(\mu\text{-}CO)\}_3(\mu_3\text{-}CH)$ (**8**), were obtained by the successive C–H/C–H and C–H/C–C bond cleavages at the μ-alkyl moiety, respectively.

Keywords: Agostic interaction; Hydrido complex; Alkyl complex; Alkyne complex; Triruthenium cluster

1. Introduction

In relation to C–H bond activation, an agostic M–H–C interaction has attracted considerable attention since the 1980s, and many studies have been published not only on monometallic complexes but also on bi- or multimetallic complexes [1]. In mononuclear complexes, the β-hydrogens are favorably disposed for formation of an agostic interaction with the metal, which often leads to β-hydrogen elimination in the case of late-metal complexes. In contrast, α-hydrogens of the alkyl group attached to one of the metal centers of a cluster are oriented to the adjacent metal center [2]. This geometrical feature of the cluster causes a different type of agostic interaction from that found in mononuclear systems, i.e. an α-C–H agostic interaction. Thus, it would be expected that reactivity of an alkyl group on a cluster is different from that of a mononuclear complex due to the effect of adjacent metal centers.

Shapley and co-workers clearly demonstrated rapid equilibrium among μ_3-methylidyne, μ_3-methylene, and μ-methyl groups in the "$Os_3(CO)_9H_n(CH_{4-n})$" ($n = 1$–3) system on the basis of the isotopic perturbation of resonance (IPR) technique [3,4]. Such transformation of a hydrocarbyl on a cluster is highly related to the activation of hydrocarbons on the cluster, and understanding the mechanistic details of the transformation is important for controlling the reactivity of the hydrocarbyls on the cluster [5]. While several complexes containing an agostic hydrocarbyl ligand have been prepared upon protonation [6,7], their isolation, which was directly formed by the reductive coupling between a

* Corresponding author. Tel.: +81 3 5734 2148; fax: +81 3 5734 3913.
E-mail address: hiroharu@n.cc.titech.ac.jp (H. Suzuki).

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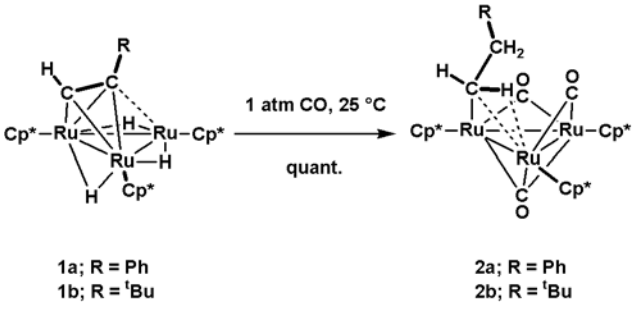
hydride and a hydrocarbyl ligand, has been quite limited [8]. We report herein synthesis of triruthenium complexes having an α-C–H agostic interaction by the reaction of μ_3-η^2:η^2(⊥)-alkyne complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}RCCH)$ (**1a**; R = Ph, **1b**; R = ^{t}Bu, $Cp^* = \eta^5\text{-}C_5Me_5$), with carbon monoxide. In this reaction, pre-equilibrium between the (⊥)-alkyne and μ_3-vinylidene structures is shown to be a key-step to form a μ-alkyl complex. The mechanistic detail of the transformation of the (⊥)-alkyne complex to a μ-alkyl complex as well as α-C–H bond and α-C–C bond cleavages of the resulting μ-alkyl ligand are also described in this report.

2. Results and discussions

Treatment of the perpendicularly coordinated alkyne complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}PhCCH)$ (**1a**) [9], with atmospheric carbon monoxide at 25 °C resulted in a quantitative formation of a μ-phenethyl complex, $(Cp^*Ru)_3(\mu\text{-}\eta^2\text{-}HCHCH_2Ph)(\mu\text{-}CO)_2(\mu_3\text{-}CO)$ (**2a**), having an α-C–H agostic interaction (Eq. (1)). The phenethyl group of **2a** was formed by migration of the three hydrido ligands of **1a** to the alkyne moiety; two of them moved to the quaternary carbon atom located inside of the Ru_3 core, and the rest migrated to the outer methine carbon atom. The vacant sites generated by the reductive C–H bond formation on the Ru_3 core were occupied by the three incoming CO molecules.



(1)

The molecular structure of **2b**, which was formed by the reaction of **1b** with CO, was determined by an X-ray diffraction study using a brown single crystal obtained from the *p*-xylene solution. Since there were two independent molecules having similar structural parameters in the unit cell, one of them is depicted in Fig. 1.

The three Ru–Ru bonds have nearly equal lengths ranging from 2.7317(5) to 2.7592(6) Å. The neohexyl group was located on the Ru(1)–Ru(3) edge, which σ-bonded to the Ru(1) atom. The Ru(3)–C(1) distance of 2.387(4) Å is considerably longer than the Ru(1)–C(1) bond length (2.124(4) Å). Such asymmetric Ru–C bond length clearly indicates η^2-coordination of the α-C–H bond to the Ru(3) atom. The bridging hydrogen atom, H(1), was successfully located during the differential Fourier synthesis, and the Ru(3)–H(1) length (1.89(6) Å) demonstrates the interaction between Ru(3) and H(1).

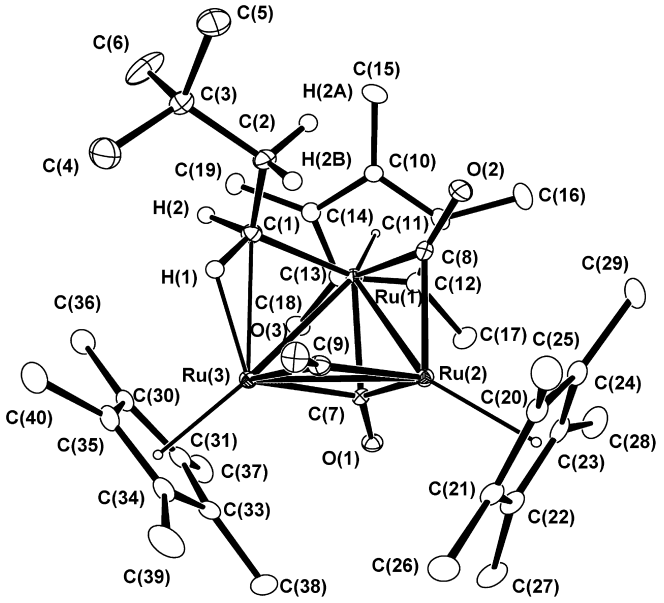
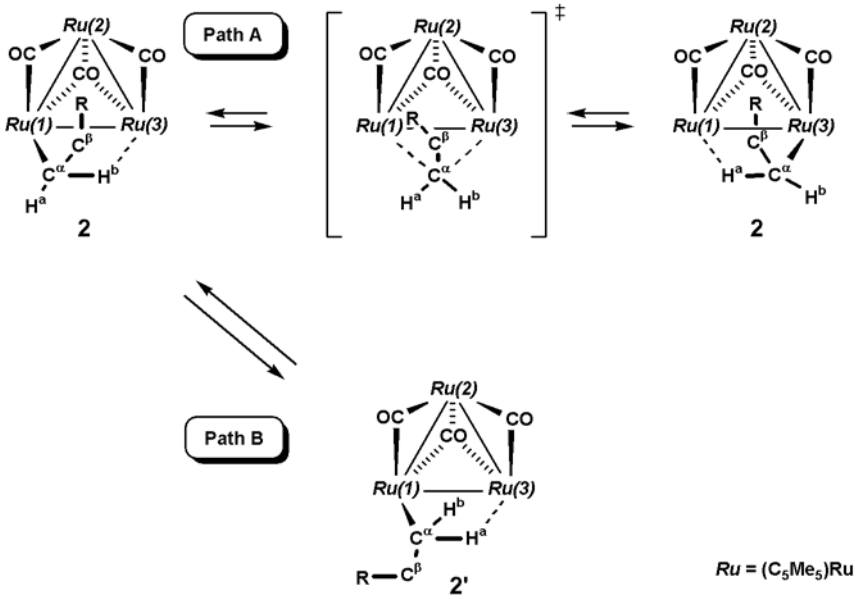


Fig. 1. Molecular Structure of **2b** with thermal ellipsoids probability at 40%. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2), 2.7349(5); Ru(1)–Ru(3), 2.7317(5); Ru(2)–Ru(3), 2.7592(6); Ru(1)–C(1), 2.124(4); Ru(1)–C(7), 2.065(4); Ru(1)–C(8), 1.998(4); Ru(2)–C(7), 2.066(3); Ru(2)–C(8), 2.030(4); Ru(2)–C(9), 1.965(4); Ru(3)–C(1), 2.387(4); Ru(3)–C(7), 2.176(4); Ru(3)–C(9), 2088(4); Ru(3)–H(1), 1.89(6); C(1)–C(2), 1.542(5); C(1)–H(1), 1.00(6); C(1)–H(2), 1.12(5); C(2)–C(3), 1.547(5); C(7)–O(1), 1.208(4); C(8)–O(2), 1.182(5); C(9)–O(3), 1.184(4); Ru(1)–Ru(2)–Ru(3), 59.629(15); Ru(1)–Ru(3)–Ru(2), 59.742(12); Ru(2)–Ru(1)–Ru(3), 60.629(14); Ru(1)–C(1)–C(2), 118.9(2).

The two carbonyl groups bridge the Ru(1)–Ru(2) and Ru(2)–Ru(3) edges, which are on the same side of the μ-neohexyl group with respect to the Ru_3 plane. The triply bridging CO group was located on the opposite face. Although there have been several structurally characterized bimetallic complexes containing an asymmetric μ-methyl ligand [6a,6f,6h,6j,10], examples of the μ-alkyl complex have been still limited [6c,6e,11]. Furthermore, the trimetallic μ-alkyl complex has been only proposed as a possible intermediate for the hydrogenation of the μ_3-alkylidyne complex [12]. To the best of our knowledge, this is the first example of a structurally well-defined trimetallic complex having an agostic μ-alkyl ligand.

As well as other homo-bimetallic complexes having an asymmetric μ-alkyl ligand [6a,6b,6d,6f,11] complex **2** exhibited rapid dynamic behavior arising from the motion of the bridging alkyl group, namely, migration of the bridging alkyl group between the Ru(1) and Ru(3) atoms through a symmetric μ-alkyl position (Scheme 1). In the ^{1}H NMR spectra of **2a** recorded at −90 °C, two broad signals and one sharp signal arising from the Cp* groups were observed at δ 1.31 ($w_{1/2}$ = 24 Hz), 1.50 ($w_{1/2}$ = 24 Hz), and 1.60 (s), respectively. With increase in the temperature, the two broad signals coalesced into one signal. At 23 °C, the time-averaged spectrum showing two sharp Cp* signals with the intensity ratio of 2:1 was obtained. Although the motion was not completely frozen even at −90 °C, free energy of activation, $\Delta G^{\ddagger}$, at the coalescence temperature



Scheme 1. Migration of the μ-alkyl group on the Ru–Ru edge.

(ca. −85 °C) was estimated at *ca*. 8.9 kcal/mol based on the difference in the chemical shifts of the two Cp^* signals.

The α-hydrogen atoms, H^a and H^b in Scheme 1, exchange the coordination sites with each other. The signals of the agostic hydrogen and the non-coordinated α-hydrogen appeared at δ −16.43 ($w_{1/2} = 31$ HZ) and 2.22 ($w_{1/2} = 44$ Hz) at −90 °C, respectively, broadened and coalesced into one signal appearing at δ −7.01 at 23 °C.

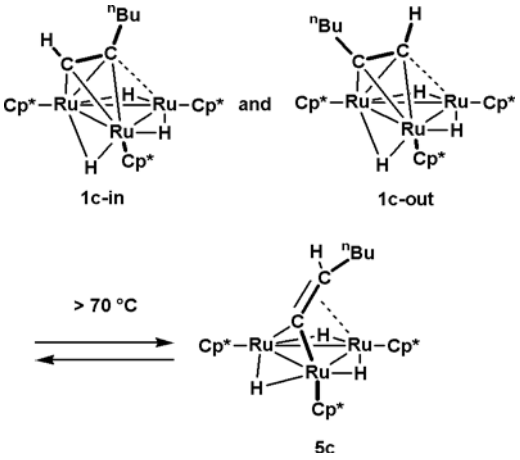
There are two possible paths for the exchange between the two α-hydrogen atoms, H^a and H^b (Scheme 1). In path A, exchange of the hydrogen atoms synchronized with the migration of the μ-alkyl groups between the two ruthenium atoms, Ru(1) and Ru(3). In contrast, path B involves rotation around the Ru(1)–C^α bond, and H^a and H^b should be diastereomerised.

Formation of diastereomers **2′** was not observed during the VT-NMR study, thus the exchange most likely proceeded by way of path A through a symmetric transition state. Lack of the diastereomer stemming from the Ru–C^α rotation is probably due to the sterical demand of the three Cp^* groups. The structure of **2** shown in Fig. 1 would be the most favorable structure due to minimized steric repulsion between the Cp^* groups and the alkyl group.

In a dimolybdenum μ-alkyl complex, $(CpMo)_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}HCHCH_2C_6H_4Me)$ ($Cp = \eta^5\text{-}C_5H_5$), similar dynamic behavior arising from the μ-alkyl migration was observed [11]. DFT calculation for the model compound suggests that the exchange of the α-hydrogen atoms proceeded through a symmetric μ-alkyl transition state rather than the $\mu\text{-}\eta^2\text{:}\eta^2$-mode (rotation around the Mo–C bond).

The ^{13}C signal of the α-carbon of **2a** was observed at δ 73.4 as a pseudo-triplet with the J_{C-H} value of 105.8 Hz. The motion of the μ-alkyl group was too fast to observe the J_{C-H} value of the agostic C–H bond directly. The J_{C-H} value for a static agostic C–H bond has been reported to range between 70 and 105 Hz [1]. The value of 105.8 Hz is quite consistent with the average of those for the terminal $C(sp^3)$–H and the agostic $C(sp^3)$–H bond.

The reaction of a 46-electron (⊥)-alkyne complex with 2e-donor often brought about transformation of a coordination mode of the alkyne ligand from perpendicular to a coordinatively saturated parallel form [13]. As mentioned in our previous communication, reaction of the (⊥)-cyclohexyne complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}cyclo\text{-}C_6H_8)$ (**3**) with CO resulted in the formation of a (//)-cyclohexyne complex, $(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{-}cyclo\text{-}C_6H_8)(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}CO)$ (**4**), with elimination of dihydrogen [14].

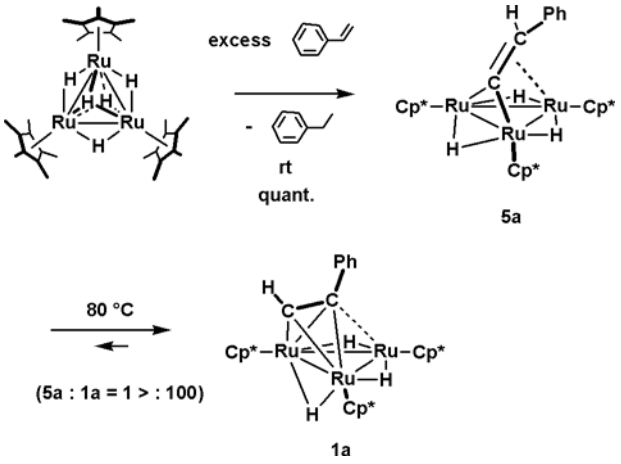


(2)

The (⊥)-alkyne complex **1** equilibrated with a μ_3-vinylidene complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{-}C{=}CRH)$ (**5**), at above 70 °C (Eq. (2)). A mixture of the 1-hexyne com-

plexes, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}HCC^nBu)$ (**1c-in** and **1c-out**), was exclusively prepared by the reaction of the pentahydrido complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$, with 1-hexyne. Complex **1c-in** possesses a butyl group at the inner acetylenic carbon atom, and **1c-out** lies in the opposite situation. These two isomers were rapidly converted between each other by way of switchback motion of the alkyne moiety at room temperature [14]. Gentle heating of **1c** afforded a mixture of **1c** and μ_3-hexenylidene complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{-}C{=}C^nBuH)$ (**5c**). Complex **5c** was alternatively synthesized by the reaction of $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ with 1-hexene in 68% yield [15], and heating of **5c** also afforded a mixture of **1c** and **5c**. The ratio between **1c** and **5c** reached 53:47 at 80 °C in 2 h. The thermodynamic parameters for the equilibrium between **5c** and **1c** was estimated at $\Delta H^0 = 6.5 \pm 1$ kcal/mol and $\Delta S^0 = 18 \pm 3$ cal mol^{-1} K^{-1} from the equilibrium constants measured at 70, 80, 90, and 100 °C.

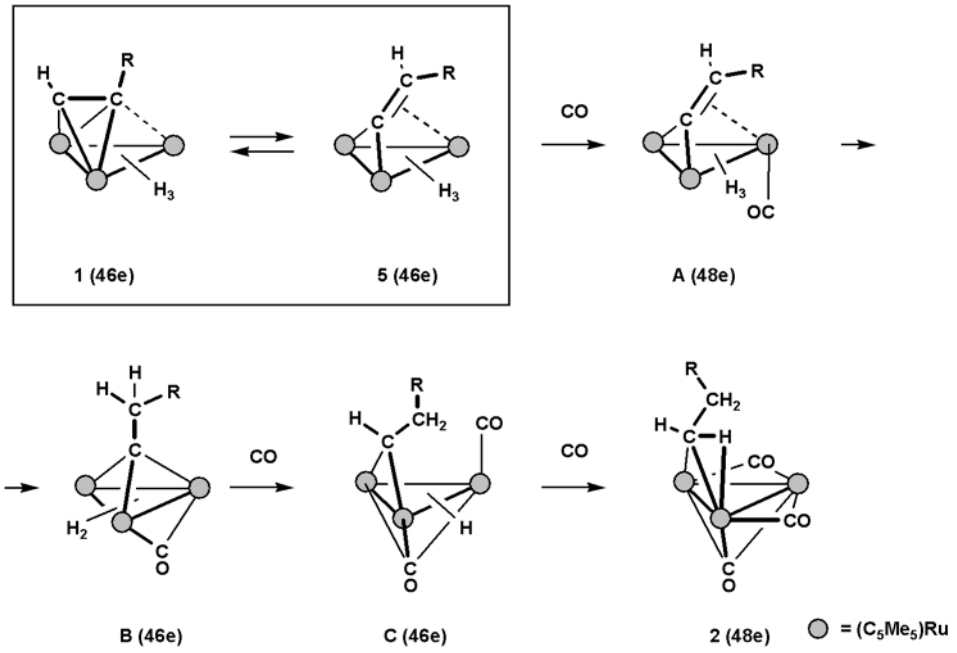
μ_3-Styrylidene complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{-}C{=}C$PhH) (**5a**), was also prepared by the reaction of the pentahydrido complex with styrene at ambient temperature, and **5a** was quantitatively converted to **1a** upon heating at 80 °C. The equilibrium between **1** and **5** was strongly affected by the size of the substituents, and a bulky substituent tilts the equilibrium in favor of the (⊥)-alkyne form. Although the signals for **5** were not observed in the ^{1}H NMR spectrum of the equilibrium mixture of **5a** and **1a**, spin saturation transfer was observed between the methine proton and the hydrido ligands of **1a** [9]. This fact indicates that there is a slight contribution of **5a** in solution.



(3)

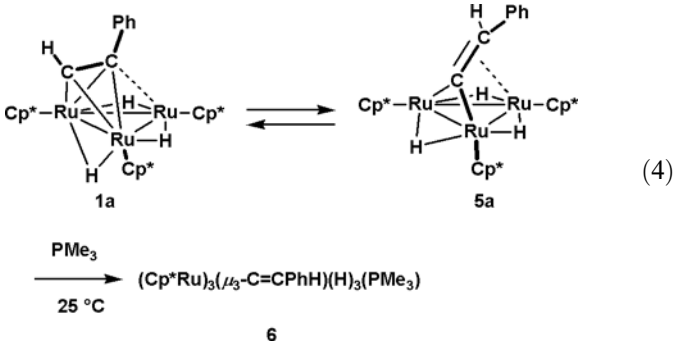
Transformation of a μ_3-alkyne ligand into a μ_3-vinylidene ligand has been often observed in the trimetallic carbonyl cluster chemistry [16]. Although mechanistic details have not yet been elucidated, it has been proposed that transformation proceeded by way of 1,2-shift of the methine proton on the C_2 moiety. However, slow exchange between the methine proton and the hydrido ligand revealed by the SST experiment strongly suggests that it was not a simple 1,2-shift of the hydrogen atom [17].

The most plausible mechanism for the formation of μ-alkyl complex **2** is shown in Scheme 2. Although both complexes **1** and **5** are coordinatively unsaturated 46-electron species, complex **5** is more reactive than **1**. While complex **1a** does not react with PMe_3 at ambient temperature, **5a** does readily react with PMe_3 to yield a 48-electron



Scheme 2. Plausible reaction mechanism of the formation of the μ-alkyl complex **2** by the reaction of **1** with carbon monoxide.

μ_3-styrylidene complex, $(Cp^*Ru)_3(\mu_3\text{-}C{=}CPhH)(H)_3(PMe_3)$ (**6**) (Eq. (4)).

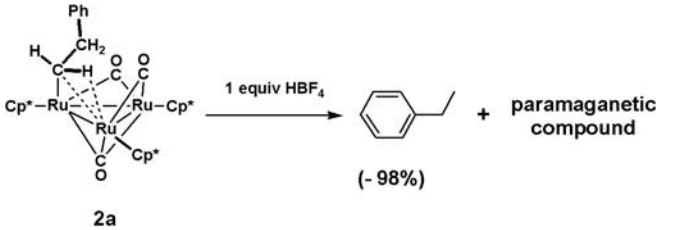


(4)

Formation of the μ_3-styrylidene ligand was well represented by the ^{13}C signals appearing at δ 265.7 (s, $^{\alpha}C$) and 79.3 (d, $J_{CH} = 155.3$ Hz, $^{\beta}C$). Three signals of the hydrido ligand were observed at δ −21.04, −17.30, and −17.16. Although formation of the coordinatively saturated phosphine adduct was confirmed by NMR spectroscopy, the position of the PMe_3 group with regard to the μ_3-vinylidene and hydrido ligands has not been elucidated at present. It is noteworthy that elimination of hydrides did not occur in this reaction and a coordinatively saturated μ_3-vinylidene species **6** was obtained.

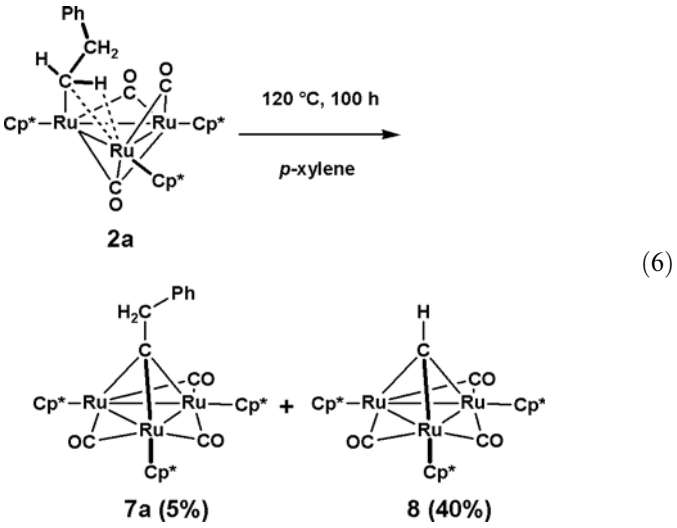
In a similar manner, the equilibrium would tilt to **5** upon treatment with CO, and lead to the formation of the μ_3-vinylidene intermediate **A**. Migration of one of the hydrido ligands to the β-carbon atom forms coordinatively unsaturated μ_3-alkylidyne intermediate **B**, which underwent addition of the second CO to form a μ-alkylidene intermediate **C**. Subsequent reductive C–H coupling concomitant with the coordination of the third CO molecule afforded **2**.

Keister and co-workers elucidated reductive C–H bond coupling between the μ_3-alkylidyne and hydrido ligands [18]. They isolated a model compound of an alkyl intermediate by introducing a heteroatom into the alkylidyne moiety [12]. Complex **2** has no hydride available to form an alkane, and the transformation should, therefore, be stopped at the μ-alkyl stage. Instead, treatment of **2a** with protic acid resulted in liberation of ethylbenzene from the Ru_3 core in nearly quantitative yield (on the basis of the ^1H NMR spectrum) as well as formation of an unidentified paramagnetic compound (Eq. (5)).



(5)

Although migratory insertion of a carbonyl ligand has been often reported [6e,f,h,j], such rearrangement was not observed for **2**. Instead, C–H and C–C bond cleavage of the μ-alkyl ligand occurred at the α-position upon pyrolysis. Heating a *p*-xylene solution of **2a** at 120 °C for 100 h resulted in complete disappearance of **2a** (Eq. (6)), and a mixture including μ_3-phenethylidyne complex, $\{Cp^*Ru(\mu\text{-}CO)\}_3(\mu_3\text{-}CCH_2Ph)$ (**7a**), μ_3-methylidyne complex, $\{Cp^*Ru(\mu\text{-}CO)\}_3(\mu_3\text{-}CH)$ (**8**), and unidentified paramagnetic compounds was obtained. Complexes **7a** and **8** were separated with column chromatography on alumina. On the basis of ^1H NMR spectra of the mixture, the yields of **7a** and **8** were estimated at 5% and 40%, respectively. Pyrolysis of **2a** in atmospheric CO resulted in an increase of **7a**.



(6)

Molecular structures of **7a** and **8** are shown in Figs. 2 and 3 along with the selected bond lengths and angles, respectively. As shown in the figures, they have quite similar structural parameters of the Ru_3C core. A distinctive feature of the structure of **7a** is the slightly long Ru(2)–Ru(3) bond (2.7464(6) Å) than other two (av. 2.709 Å), while the Ru–Ru bonds of **8** show almost the same values (av. 2.708 Å). The μ_3-phenethyl group was inclined to the Ru(2)–Ru(3) edge. The steric repulsion between the phenethyl group and the Cp^* groups on Ru(2) and Ru(3) would cause elongation of the Ru(2)–Ru(3) bond.

There have been several examples of the structurally characterized triruthenium complex having a μ_3-CR (R=H, alkyl, aryl) ligand [19]. Among them, a closely related μ_3-ethylidyne complex, $\{Cp^*Ru(\mu\text{-}CO)\}_3(\mu_3\text{-}CMe)$, has been synthesized by Knox and co-workers [19e]. They studied electrochemical oxidation of the μ_3-ethylidyne complex leading to the formation of a monocationic μ_3-vinylidene complex, and performed a diffraction study for a paramagnetic intermediate, $[\{Cp^*Ru(\mu\text{-}CO)\}_3(\mu_3\text{-}CMe)](BF_4)$, having a μ_3-ethylidyne ligand. The paramagnetic complex has almost the same structural parameters as **7a** and **8**. A μ_3-benzylidyne complex with the Cp_3Ru_3 version has been prepared [19h], whose structural parameters were also nearly equal to those of **7a** and **8**.

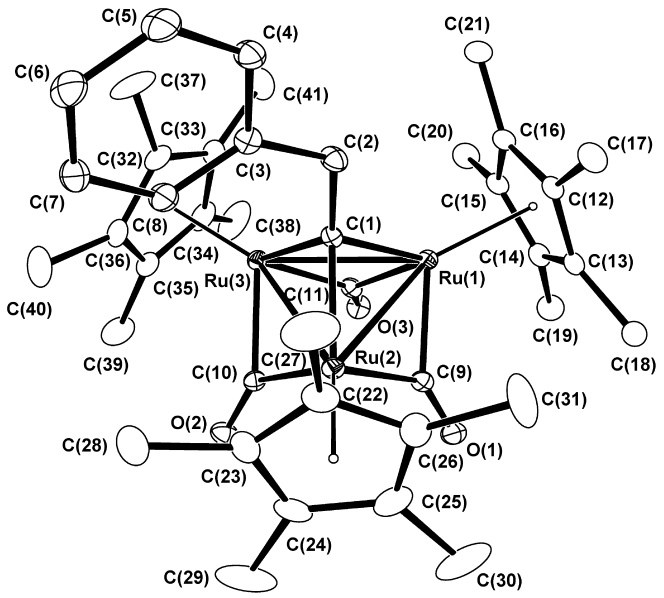


Fig. 2. Molecular structure of **7a** with thermal ellipsoids probability at 30% level. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2), 2.7095(6); Ru(2)–Ru(3), 2.7464(6); Ru(1)–Ru(3), 2.7081(5); Ru(1)–C(1), 2.026(4); Ru(2)–C(1), 2.028(4); Ru(3)–C(1), 2.023(4); Ru(1)–C(9), 1.998(4); Ru(2)–C(9), 2.025(4); Ru(2)–C(10), 2.032(4); Ru(3)–C(10), 2.016(4); Ru(3)–C(11), 2.032(4); Ru(1)–C(11), 1.999(4); C(1)–C(2), 1.511(6); C(2)–C(3), 1.511(6); C(9)–O(1), 1.179(5); C(10)–O(2), 1.179(5); C(11)–O(3), 1.176(5); Ru(1)–Ru(2)–Ru(3), 59.515(16); Ru(2)–Ru(3)–Ru(1), 59.564(14); Ru(2)–Ru(1)–Ru(3), 60.921(14).

During the formation of **7a** and **8**, the agostic C–H bond at the α-carbon of **2a** was cleaved. Although mechanistic details have not yet been elucidated, they would be formed via the formation of a μ-phenethylidene intermediate **D** (Scheme 3). There were two possible structures for the μ-phenethylidene intermediate in regard to the orientation of the phenethyl group; **D-in** possess a phenethyl group inside of the Ru_3 core and **D-out** adopts an opposite orientation. Further C–H or C–C bond activation would occur at the ruthenium center, to which the μ-alkylidene was not attached. C–C bond activation seems to be preferable in **D-in**, and C–H bond cleavage should be favorable in **D-out**. The intermediate **D-in** would equilibrate with **D-out** by way of a pivot motion of the μ-alkylidene ligand. Such pivot motion of a doubly bridging ligand has been reported [20,21].

Formation of **8** by way of C–C bond cleavage was favored rather than the C–H bond cleavage leading to the formation of **7a**. It is probably due to the thermodynamic stability of **D-in** in comparison to **D-out**. Since the phenethyl group orients to inside of the Ru_3 core in **D-in**, steric repulsion between the phenethyl group and the Cp^* groups is considerably reduced.

The reaction of **1d** containing a less bulkier substituent, ^{n}Pr group, with 1 atm of CO at 25 °C also resulted in the formation of μ-pentyl complex **2d** and μ_3-pentylidyne complex **7d** in 9% and 91% yield, respectively (Eq. (7)). Although the minor product **2d** was not isolated, a broad signal appearing at δ −7.15 in the ^{1}H NMR spectrum of the mixture of **2d** and **7d** strongly suggests the formation of the μ-η^2-alkyl complex with C–H agostic interaction. The chemical shift of δ −7.15 for **2d** is similar to those of α-agostic hydrogen atoms in **2a** (δ −7.01) and **2b** (δ −7.15).

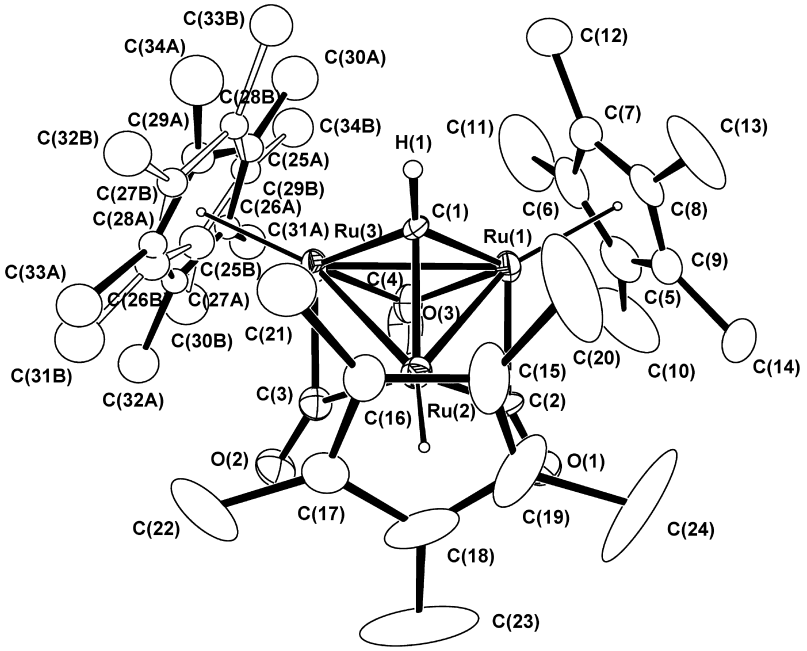
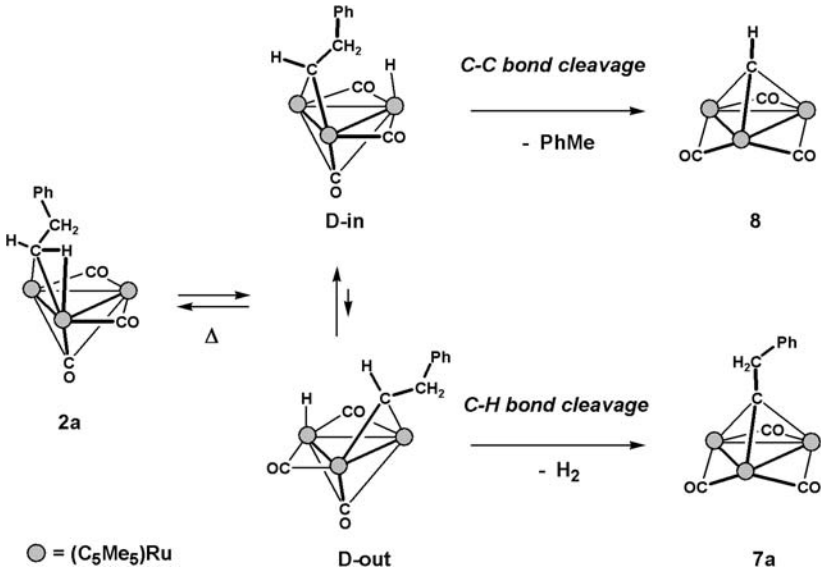
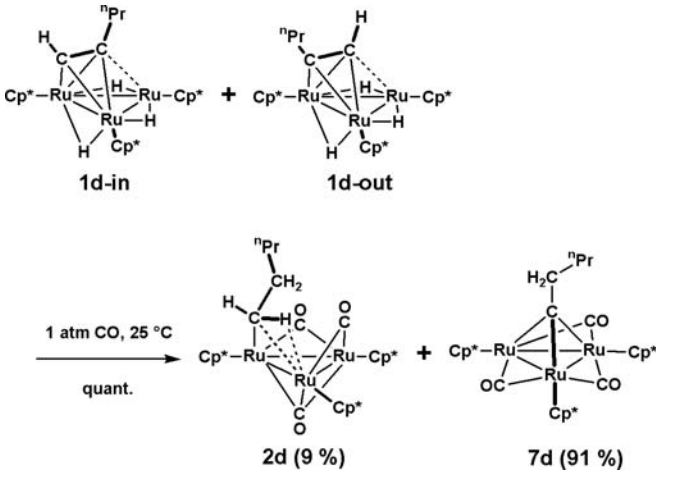


Fig. 3. Molecular structure of **8** with thermal ellipsoids probability at 30% level. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2), 2.7064(11); Ru(1)–Ru(3), 2.7110(10); Ru(2)–Ru(3), 2.7052(12); Ru(1)–C(1), 1.997(6); Ru(1)–C(2), 2.033(6); Ru(1)–C(4), 2.018(7); Ru(2)–C(1), 2.013(6); Ru(2)–C(2), 2.049(6); Ru(2)–C(3), 2.020(6); Ru(3)–C(1), 1.996(6); Ru(3)–C(3), 2.027(7); Ru(3)–C(4), 2.025(7); C(2)–O(1), 1.152(7); C(3)–O(2), 1.174(8); C(4)–O(3), 1.181(9); Ru(1)–Ru(2)–Ru(3), 60.13(3); Ru(1)–Ru(3)–Ru(2), 59.96(2); Ru(2)–Ru(1)–Ru(3), 59.91(3).



Scheme 3. Plausible mechanism of the formation of **7a** and **8** upon thermolysis of **2a**.



(7)

Complex **7d** was isolated using column chromatography on alumina and fully characterized on the basis of ^{1}H and ^{13}C NMR, and IR spectra as well as elemental analysis. A ^{13}C signal ascribed to the three bridging carbonyl ligands was observed at δ 247.0, which showed that there is a three-folded axis of symmetry in complex **7d**. The μ_3-pentylidyne carbon was observed at δ 320.4, which is characteristic of a triply bridging carbon atom.

In this reaction, the μ_3-methylidyne complex **8** as a consequence of C–C bond cleavage was not formed. This is consistent with the assumption that the reaction was controlled by the stability of the μ-alkylidene intermediate. Since intermediate **D-out** is relatively stabilized due to the reduction of the steric repulsion, a more feasible C–H bond cleavage leading to the μ_3-pentylidyne skeleton would predominantly occur. This would also cause the smooth reaction to the μ_3-alkylidyne complex even at room temperature. Gentle heating of the mixture at 60 °C resulted in quantitative conversion of **2d** to **7d**.

3. Conclusion

In summary, while the reaction of a (⊥)-alkyne complex with 2e-donors has often resulted in the formation of a coordinatively saturated (//)-alkyne complex as found in the literature [13] and $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2{:}\eta^2(\perp)\text{-}cyclo\text{-}C_6H_8)$ (**3**) [14], the reaction of **1** with CO afforded triruthenium complex **2** having a μ-alkyl ligand instead of a (//)-alkyne complex. The equilibrium between the (⊥)-alkyne and the μ_3-vinylidene forms, and high reactivity of the μ_3-vinylidene complex **5** would lead to the formation of a μ-alkyl complex.

Similar to other bimetallic complexes having an asymmetric μ-alkyl ligand, complex **2** exhibits a dynamic behavior in solution. This dynamic process brought about site-exchange of the α-hydrogen atoms between the terminal and bridging positions, which was synchronized with the migration of the μ-alkyl groups between the two ruthenium atoms.

Pyrolysis of the μ-phenethyl complex **2a** resulted in the formation of μ_3-phenethylidyne complex **7a** and μ_3-methylidyne complex **8**. Formation of **7a** is regarded as a model of the alkane activation performed by the triruthenium μ_3-sulfido complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}S)$, to yield a μ_3-alkylidyne complex [19k].

As mentioned in our previous communication, the (⊥)-alkyne complex **1** was observed as an intermediate during the reaction of the triruthenium pentahydrido complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$, with linear alkane yielding a *closo*-ruthenacyclopentadiene complex, $(Cp^*Ru)_2\{Cp^*Ru(\text{–}CR{=}CH\text{–}CH{=}CH\text{—})\}(\mu\text{-}H)$ [22]. The equilibrium between **1** and **5** is affected by the nature of the substituents on the C_2 moiety, namely, bulky substituents tilt the equilibrium toward the (⊥)-alkyne structure. We are currently investigating the effect of the electronic nature of the metal

centers on the equilibrium between the (⊥)-alkyne and μ_3-vinylidene complexes as well as further skeletal rearrangement of the μ_3-vinylidene complex at higher temperature range.

4. Experimental

4.1. General procedures

All experiments were carried out under an argon atmosphere. All compounds were treated with Schlenk techniques. Dry toluene, tetrahydrofuran, and pentane used in this study were purchased from Kanto Chemicals. Benzene-d_6, tetrahydrofuran-d_8, and toluene-d_8 were dried over sodium-benzophenone ketyl and stored under an argon atmosphere. CD_2Cl_2 was dried over diphosphorus pentoxide and stored under an argon atmosphere. μ_3-Alkyne complexes $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}RCCH)$ (**1a**; R=Ph, **1b**; R = ^{t}Bu) were prepared according to a published method [9]. IR spectra were recorded on a Nicolet AVATAR 360 E.S.P. spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 and JEOL GSX-500 spectrometer with TMS as an internal standard. ^{31}P NMR spectra were recorded on a Varian INOVA-400 spectrometer with H_3PO_4 as an internal standard. Elemental analyses were performed by the Perkin–Elmer 2400 II instrument.

4.2. X-ray crystallography

Single crystals of α-*agostic* neohexyl complex **2b**, μ_3-phenethylidyne complex **7a**, and μ_3-methylidyne complex **8** were obtained directly from the preparations described below and mounted on glass fibers or on the cryoloop. Diffraction experiments of **2b**, **7a**, and **8** were performed on a Rigaku R-AXIS RAPID imaging plate with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structures of **2b**, **7a**, and **8** were solved by the Patterson method and subsequent Fourier difference techniques using SHELX-97 program package. All non-hydrogen atoms were refined anisotropically by least squares calculation on F^2. The hydrogen atoms, H(1) and H(2), bonded to the bridging carbon atom, C(1), in **2b** were successfully located during the Fourier synthesis and refined isotropically. Neutral atom scattering factors were obtained from the standard sources [23]. Crystal data and results of the analyses are listed in Table 1.

Table 1
Crystallographic details of **2b**, **7a**, and **8**

	2b	**7a**	**8**
Empirical formula	$C_{39}H_{58}O_3Ru_3$	$C_{41}H_{52}O_3Ru_3{\cdot}0.5C_7H_8$	$C_{34}H_{46}O_3Ru_3$
Formula weight	878.06	942.10	805.92
Crystal color	Brown	Red	Red
Crystal size (mm)	$0.27 \times 0.06 \times 0.02$	$0.40 \times 0.08 \times 0.04$	$0.10 \times 0.10 \times 0.05$
Crystallizing solution (temp.)	*p*-Xylene-d_{10} (23 °C)	Toluene (−15 °C)	C_6D_6 (23 °C)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (#2)	$P2/c$ (#13)	$P\bar{1}$ (#2)
a (Å)	10.947(2)	20.358(4)	8.415(3)
b (Å)	17.928(3)	9.0806(13)	11.072(5)
c (Å)	19.578(3)	21.157(3)	18.021(5)
α (°)	82.308(7)		90.020(14)
β (°)	87.754(8)	100.974(8)	94.079(11)
γ (°)	88.688(8)		108.299(15)
Volume (Å^3)	3804.3(11)	3839.7(11)	1589.6(10)
Z value	4	4	2
D_{calc} (g/cm^3)	1.533	1.630	1.684
Measurement temp. (°C)	−150	−120	−50
μ (Mo Kα) (mm^{-1})	1.209	1.205	1.439
2θ max (°)	60.0	60.0	60.0
No. of data collected	43560	46518	19323
No. of unique data	21847 ($R_{int} = 0.0298$)	11856 ($R_{int} = 0.0686$)	9168 ($R_{int} = 0.0521$)
No. of unique data with $I_0 > 2\sigma(I_0)$	18041	8460	6361
No. of parameters	864	464	367
Abs. correction type	Numerical	Empirical	Empirical
Abs. transmission	0.8133 (min.)	0.6597 (min.)	0.5957 (min.)
	1.0000 (max.)	1.0000 (max.)	1.0000 (max.)
$R_1(I > 2\sigma(I))$	0.0410	0.0484	0.0630
$wR_2(I > 2\sigma(I))$	0.1108	0.1045	0.1501
R_1 (all data)	0.0521	0.0720	0.0948
wR_2 (all data)	0.1171	0.1175	0.1733
GOF	1.041	1.035	1.073
Highest diff. peak (e Å^{-3})	5.396	2.855	1.453
Deepest hole	−0.990	−1.230	−1.907

4.3. $(Cp^*Ru)_3(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu\text{-}\eta^2\text{-}HCHCH_2Ph)$ (**2a**)

A 50 mL Schlenk tube was charged with a μ_3-phenylacetylene complex **1a** (22.7 mg, 31.8 μmol) and pentane (2 mL). The reaction solution was frozen by the use of a liquid-nitrogen bath, and then the tube was evacuated. After the tube was warmed up to 25 °C, 1 atm of CO was introduced into the tube. The solution was stirred vigorously for 62 h at 25 °C. The color of the solution turned from dark-green to brown. The solvent was removed under reduced pressure, and **2a** was obtained as a brown crystalline solid (25.3 mg, 88.5% yield). ^{1}H NMR (400 MHz, THF-d_8, 23 °C): δ −7.01 (br, $w_{1/2} = 35$ Hz, 2H, Ru–CH_2–), 1.43 (s, 30H, C_5Me_5), 1.58 (s, 15H, C_5Me_5), 2.27 (t, $J_{H-H} = 6.3$ Hz, 2H, –CH_2Ph), 6.95 (t, $J_{H-H} = 7.2$ Hz, 1H, *p-Ph*), 7.00 (d, $J_{H-H} = 7.2$ Hz, 2H, *o-Ph*), 7.07 (t, $J_{H-H} = 7.2$ Hz, 2H, *m-Ph*). ^{1}H NMR (500 MHz, THF-d_8, −90 °C): δ −16.43 (br, $w_{1/2} = 31$ Hz, 1H, Ru–*H*CH–), 1.31 (br, $w_{1/2} = 24$ Hz, 15H, C_5Me_5), 1.50 (br, $w_{1/2} = 24$ Hz, 15H, C_5Me_5), 1.60 (s, 15H, C_5Me_5), 2.05 (br, $w_{1/2} = 50$ Hz, 1H, –CH_2Ph), 2.22 (br, $w_{1/2} = 44$ Hz, 1H, Ru–HC*H*–), 2.36 (br, $w_{1/2} = 38$ Hz, 1H, –CH_2Ph), 7.00 (t, $J_{H-H} = 6.8$ Hz, 1H, *p-Ph*), 7.02 (d, $J_{H-H} = 7.6$ Hz, 2H, *o–Ph*), 7.12 (t, $J_{H-H} = 7.2$ Hz, 2H, *m–Ph*). ^{13}C NMR (100 MHz, THF-d_8, 23 °C): δ 9.2 (q, $J_{C-H} = 126.8$ Hz, C_5Me_5), 9.3 (q, $J_{C-H} = 127.3$ Hz, C_5Me_5), 41.3 (t, $J_{C-H} = 130.0$ Hz, –*C*H_2Ph), 73.4 (t, $J_{C-H} = 105.8$ Hz, Ru–*C*H_2–), 98.8 (s, C_5Me$_5$), 102.2 (s, C_5Me$_5$), 126.0 (d, $J_{C-H} = 159.0$ Hz, *Ph*), 128.9 (d, $J_{C-H} = 158.8$ Hz, *Ph*), 129.5 (d, $J_{C-H} = 155.3$ Hz, *Ph*), 148.2 (s, *ipso-Ph*), 253.4 (s, μ-CO), 263.5 (s, μ_3-CO). ^{13}C NMR (125 MHz, THF-d_8, −90 °C): δ 9.2 (q, $J_{C-H} = 126.8$ Hz, C_5Me_5), 9.3 (q, $J_{C-H} = 127.3$ Hz, C_5Me_5), 41.8 (t, $J_{C-H} = 131.8$ Hz, –*C*H_2Ph), 78.1 (unresolved dd, Ru–H*C*H–), 97.1 (br, $w_{1/2} = 65$ Hz, C_5Me$_5$), 100.0 (br, $w_{1/2} = 65$ Hz, C_5Me$_5$), 101.7 (s, C_5Me$_5$), 126.1 (d, $J_{C-H} = 160.4$ Hz, *Ph*), 129.0 (d, $J_{C-H} = 155.4$ Hz, *Ph*), 129.5 (d, $J_{C-H} = 157.6$ Hz, *Ph*), 148.0 (s, *ipso-Ph*), 252.4 (br, $w_{1/2} = 59$ Hz, μ-CO), 258.4 (br, $w_{1/2} = 60$ Hz, μ-CO), 264.0 (s, μ_3-CO). IR (KBr, cm^{-1}): 2963, 2904, 1758 (μ-CO), 1723 (μ-CO), 1611 (μ_3-CO), 1492, 1451, 1371, 1070, 1025, 755. Anal. Calc. for $C_{41}H_{54}O_3Ru_3$: C, 54.82; H, 6.07. Found: C, 54.70; H, 5.82%.

4.4. $(Cp^*Ru)_3(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu\text{-}\eta^2\text{-}HCHCH_2{}^tBu)$ (**2b**)

A 50 mL Schlenk tube was charged with a μ_3-*tert*-butylacetylene complex **1b** (11.4 mg, 14.4 μmol) and pentane (2 mL). The reaction solution was frozen by the use of a liquid-nitrogen bath, and then the tube was evacuated. After the tube was warmed up to 25 °C, 1 atm of CO was introduced into the tube. The solution was stirred vigorously for 62 h at 25 °C. The color of the solution turned from brown to dark-brown. The solvent was removed under reduced pressure, and **2b** was obtained as a brown solid (10.7 mg, 84.9% yield). A brown single crystal suitable for the X-ray diffraction study was obtained from a *p*-xylene solution placed at 23 °C. ^{1}H NMR (400 MHz, THF-d_8, 23 °C): δ −7.15 (s, 2H, Ru–CH_2–), 0.84 (s, 9H, *t-Bu*), 1.06 (s, $J_{H-H} = 5.6$ Hz, 2H, –CH_2-*t*-Bu), 1.60 (s, 30H, C_5Me_5), 1.67 (s, 15H, C_5Me_5). ^{13}C NMR (100 MHz, THF-d_8, 23 °C): δ 9.0 (q, $J_{C-H} = 127.2$ Hz, C_5Me_5), 9.3 (q, $J_{C-H} = 126.7$ Hz, C_5Me_5), 30.2 (q, $J_{C-H} = 129.0$ Hz, –C*Me*$_3$), 49.3 (t, $J_{C-H} = 127.8$ Hz, –C$H_2{}^t$Bu), 60.3 (t, $J_{C-H} = 101.8$ Hz, Ru–CH_2–), 98.6 (s, C_5Me$_5$), 102.2 (s, C_5Me$_5$), 251.9 (s, μ-*C*O), 263.3 (s, μ_3-*C*O). IR (NaCl, cm^{-1}): 2904, 1753 (μ-CO), 1719 (μ-CO), 1618 (μ_3-CO), 1474, 1452, 1374, 1157, 1076, 1023, 954, 868. Anal. Calc. for $C_{39}H_{58}O_3Ru_3$: C, 53.17; H, 6.67. Found: C, 53.35; H, 6.66%.

4.5. $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2{:}\eta^2(\perp)\text{-}RCCH)$ (**1c**; $R = {}^nBu$, **1d**; ${}^nPr$)

A 50 mL Schlenk tube was charged with the pentahydrido complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}H)_2$ (93.6 mg, 0.131 mmol), 1-pentyne (15.5 μL, 0.157 mmol), and THF (8 mL). The solution was stirred vigorously for 10 min at 25 °C. The color of the solution turned from dark-purple to dark-brown. The solvent was removed under reduced pressure and the residual solid was purified by the use of column chromatography on alumina (Merck Art. No. 1097) with toluene. The solvent was removed under reduced pressure and an equilibrating mixture, **1d-in** and **1d-out**, was obtained as a dark-green solid (60.6 mg, 59.2% yield). The ratio between **1d-in** and **1d-out** was estimated at 100:48 at −50 °C on the basis of the ^{1}H NMR spectrum of the mixture. Complex **1c** was prepared from the reaction of $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}H)_2$ (175.8 mg, 0.246 mmol) with 1-hexyne (34.0 μL, 0.296 mmol) in a similar manner, and isolated in 63.0% yield (123.0 mg). The ratio between **1c-in** and **1c-out** was estimated at 100:62 at −50 °C on the basis of the ^{1}H NMR spectrum of the mixture.

1d-in: ^{1}H NMR (400 MHz, toluene-d_8, −50 °C): δ −24.74 (t, $J_{H-H} = 3.1$ Hz, 1H, Ru–*H*), −6.47 (d, $J_{H-H} = 3.1$ Hz, 2H, Ru–*H*), 0.94 (t, $J_{H-H} = 7.2$ Hz, 3H, –CH_3), 1.88 (s, 30H, C_5Me_5), 1.97 (s, 15H, C_5Me_5), 10.16 (s, 1H, ^{n}PrCC*H*). Broad signals, which were derived from –CH_2– groups of the *n*-propyl groups of **1d-in** and **1d-out**, were observed in the region from δ 0.6 to 1.7, but assignment to each isomer cannot be done due to complexity of the signals. ^{13}C NMR (100 MHz, toluene-d_8, −50 °C): δ 11.9 (q, $J_{CH} = 126.2$ Hz, C_5Me_5), 12.6 (q, $J_{C-H} = 126.1$ Hz, C_5Me_5), 15.0 (q, $J_{C-H} = 121.5$ Hz, –*C*H_3), 25.7 (t, $J_{C-H} = 130.4$ Hz, –*C*H_2–), 36.1 (t, $J_{C-H} = 129.0$ Hz, –*C*H_2–), 67.0 (s, ^{n}Pr*C*CH), 84.2 (s, C_5Me$_5$), 89.1 (s, C_5Me$_5$), 178.5 (d, $J_{C-H} = 178.2$ Hz, ^{n}PrC*C*H). **1d-out**; ^{1}H NMR (400 MHz, toluene-d_8, −50 °C): δ −25.78 (t, $J_{H-H} = 3.6$ Hz, 1H, Ru–*H*), −11.44 (d, $J_{H-H} = 3.6$ Hz, 2H, Ru–*H*), 0.34 (s, 1H, *H*CC^{n}Pr), 1.33 (t, 3H, –CH_3), 1.80 (s, 30H, C_5Me_5), 2.07 (s, 15H, C_5Me_5). Broad signals, which were derived from –CH_2– groups of the *n*-propyl groups of **1d-in** and **1d-out**, were observed in the region from δ 0.6 to 1.7, but assignment to each isomer cannot be done due to complexity of the signals. ^{13}C NMR (100 MHz,

toluene-d_8, −50 °C): δ 12.6 (q, J_{C-H} = 126.1 Hz, C_5Me_5), 13.7 (q, J_{C-H} = 125.7 Hz, C_5Me_5), 15.7 (q, J_{C-H} = 121.8 Hz, –CH_3), 26.7 (t, J_{C-H} = 126.6 Hz, –CH_2–), 43.9 (t, J_{C-H} = 123.6 Hz, –CH_2–), 63.6 (d, J_{C-H} = 153.4 Hz, HCC^nPr), 84.7 (s, C_5Me_5), 90.4 (s, C_5Me_5), 186.7 (s, HCC^nPr). **1d-in** and **1d-out**; IR (ATR, cm^{-1}): 2953, 2896, 1473, 1455, 1424, 1371, 1025. Anal. Calc. for $C_{35}H_{56}Ru_3$: C, 53.89; H, 7.24. Found: C, 54.05, H, 7.34%.

1c-in: ^{1}H NMR (400 MHz, toluene-d_8, −50 °C): δ −24.75 (t, J_{H-H} = 2.8 Hz, 1H, Ru–*H*), −6.51 (d, J_{H-H} = 2.8 Hz, 2H, Ru–*H*), 0.97 (t, J_{H-H} = 6.9 Hz, 3H, –CH_3), 1.89 (s, 30H, C_5Me_5), 1.97 (s, 15H, C_5Me_5), 10.19 (s, 1H, ^{n}BuCC*H*). Broad signals, which were derived from –CH_2– groups of the *n*-butyl groups of **1c-in** and **1c-out**, were observed in the region from δ 0.5 to 1.4, but assignment to each isomer cannot be done due to complexity of the signals. $^{13}C\{^1H\}$ NMR (100 MHz, toluene-d_8, −50 °C): δ 12.6 (C_5Me_5), 13.7 (C_5Me_5), 15.3 (–CH_3), 23.8 (–CH_2–), 33.6 (–CH_2–), 36.5 (–CH_2–), 65.6 (s, ^{n}Bu*C*CH), 84.2 (C_5Me_5), 89.1 (C_5Me_5), 178.5 (^{n}BuC*C*H). **1c-out**; ^{1}H NMR (400 MHz, toluene-d_8, −50 °C): δ −25.77 (t, J_{H-H} = 3.6 Hz, 1H, Ru–*H*), −11.44 (d, J_{H-H} = 3.6 Hz, 2H, Ru–*H*), 0.27 (s, 1H, *H*CC^nBu), 1.33 (t, 3H, –CH_3), 1.82 (s, 30H, C_5Me_5), 2.07 (s, 15H, C_5Me_5). Broad signals, which were derived from –CH_2– groups of the *n*-butyl groups of **1c-in** and **1c-out**, were observed in the region from δ 0.5 to 1.4, but assignment to each isomer cannot be done due to complexity of the signals. $^{13}C\{^1H\}$ NMR (100 MHz, toluene-d_8, −50 °C): δ 12.0 (C_5Me_5), 12.6 (C_5Me_5), 15.1 (–CH_3), 24.6 (–CH_2–), 35.7 (–CH_2–), 41.7 (–CH_2–), 63.1 (HCC^nBu), 84.7 (s, C_5Me_5), 90.4 (s, C_5Me_5), 186.7 (HCC^nBu). **1c-in** and **1c-out**; IR (ATR, cm^{-1}): 2973, 2899, 1455, 1424, 1371, 1025, 866. Anal. Calc. for $C_{36}H_{58}Ru_3$: C, 54.45; H, 7.36. Found: C, 54.19, H, 7.30%.

4.6. Reaction of $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}^nPrCCH)$ (*1d-in* and *1d-out*) with CO

A 50 mL Schlenk tube was charged with a μ_3-1-pentyne complex **1d** (23.2 mg, 29.7 μmol) and toluene (2 mL). The reaction solution was frozen by the use of a liquid-nitrogen bath, and then the tube was evacuated. After the tube was warmed up to 25 °C, 1 atm of CO was introduced into the tube. The solution was stirred vigorously for 2 h at 25 °C. The color of the solution turned from dark-green to red-brown. The solvent was removed under reduced pressure, and the mixture of **2d** and **7d** (**2d**:**7d** = 9 : 91) was obtained as a red-brown solid. Complex **7d** was purified by the use of column chromatography on alumina (Merck Art. No. 1097) with THF. The second red band was collected and complex **7d** was obtained as a red crystalline solid by removal of the solvent (15.0 mg, 58.6% yield). **2d**; ^{1}H NMR (400 MHz, THF-d_8, 23 °C): δ −7.15 (br s, $w_{1/2}$ = 14.3 Hz, Ru–CH_2–). **7d**; ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ 1.27 (t, J_{H-H} = 6.9 Hz, 3H, –CH_3), 1.68 (s, 45H, C_5Me_5), 1.82 (m, 2H, –CH_2–), 2.35 (m, 2H, –CH_2–), 4.73 (t, J_{H-H} = 8.4 Hz, 2H, –CH_2–). ^{13}C NMR (100 MHz, C_6D_6, 23 °C): δ 7.8 (q, J_{CH} = 126.9 Hz, C_5Me_5), 12.7 (q, J_{C-H} = 124.1 Hz, –CH_3), 22.0 (t, J_{C-H} = 124.1 Hz, –CH_2–), 34.0 (t, J_{C-H} = 127.4 Hz, –CH_2–), 55.5 (t, J_{C-H} = 123.6 Hz, –CH_2–), 98.6 (s, C_5Me_5), 247.0 (s, μ-*C*O), 320.4 (s, μ_3-*C*–). IR (NaCl, cm^{-1}): 2908, 1783, 1736, 1459, 1376, 1138, 1071, 1026, 920, 795. Anal. Calc. for $C_{38}H_{54}O_3Ru_3$: C, 52.94; H, 6.33. Found: C, 52.48, H, 6.07%.

4.7. Thermolysis of the mixture obtained from the reaction of *1d* with CO

A 4.4 mg of the crude product obtained in Section 4.6 (including **2d** and **7d** with the ratio of 9:91) was charged in an NMR tube with 0.4 mL of C_6D_6. After hexamethylbenzene (2.1 mg, 12.6 μmol) was introduced in the NMR tube as an internal standard, the tube was sealed. Then, the NMR tube was heated in an oil-bath at 60 °C for 84 h. Quantitative conversion of **2d** into **7d** was observed by the use of ^{1}H NMR spectroscopy.

4.8. $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{-}C{=}C^nBuH)$ (*5c*)

A 50 mL Schlenk tube was charged with the pentahydrido complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}H)_2$ (131.8 mg, 0.184 mmol), 1-hexene (2 mL, 17.4 mmol), and THF (10 mL). The solution was stirred vigorously for 40 h at 25 °C. The color of the solution turned from dark-purple to dark-brown. The solvent was removed under reduced pressure and the residual solid was purified by the use of column chromatography on alumina (Merck Art. No. 1097) with toluene. The solvent was removed under reduced pressure and **5c** was obtained as a dark-brown solid (99.3 mg, 68.0% yield). ^{1}H NMR (400 MHz, toluene-d_8, 23 °C): δ −18.53 (d, J_{H-H} = 3.3 Hz, 1H, Ru–*H*), −17.21 (d, J_{H-H} = 4.9 Hz, 1H, Ru–*H*), −11.28 (dd, J_{H-H} = 4.9, 3.3 Hz, 1H, Ru–*H*), 0.99 (t, J_{H-H} = 7.0 Hz, 3H, –^{6}CH_3), 1.22–1.37 (m, 2H, –^{4}CH_2–), 1.38–1.55(m, 2H, –^{5}CH_2–), 1.74 (s, 15H, C_5Me_5), 1.82 (s, 15H, C_5Me_5), 1.83 (s, 15H, C_5Me_5), 2.28 (m, 2H, –^{3}CH_2–), 4.45 (dd, J_{H-H} = 9.9, 2.4 Hz, 1H, μ_3-CC^{n}Bu*H*). ^{13}C NMR (100 MHz, toluene-d_8, 23 °C): δ 11.8 (q, J_{C-H} = 126.6 Hz, C_5Me_5), 12.5 (q, J_{C-H} = 126.1 Hz, C_5Me_5), 13.1 (q, J_{C-H} = 126.4 Hz, C_5Me_5), 14.8 (q, J_{C-H} = 125.3 Hz, –^{6}CH_3), 23.3 (t, J_{C-H} = 123.6 Hz, –^{5}CH_2–), 38.1 (t, J_{C-H} = 123.7 Hz, –^{4}CH_2– and –^{3}CH_2–), 79.3 (d, J_{C-H} = 154.9 Hz, μ_3-C=^{2}C^{n}BuH), 89.5 (s, C_5Me_5), 90.7 (s, C_5Me_5), 91.0 (s, C_5Me_5), 326.3 (s, μ_3-^{1}C=C^{n}BuH).

4.9. VT-NMR study of the mixture of *1c* and *5c*

An NMR tube was charged with **1c** (14.4 mg, 18.1 μmol), toluene-d_8 (0.4 mL), and cyclooctane (0.5 μL) as an internal standard. The NMR tube was sealed, and then heated above 70 °C in an NMR probe. The reaction was monitored by the use of ^{1}H NMR spectroscopy, and proceeded until the **5c**/**1c** ratio became constant. The mole

ratio between **5c** and **1c** was determined from intensity of the Cp^* signals of these complexes. The experiments were carried out at 100, 90, 80, and 70 °C, respectively. Results are summarized in Supporting Information (Table S-1).

4.10. {$Cp^*Ru(\mu\text{-}H)\}_3$ (μ_3-η^2-C═CPhH) (**5a**)

A 50 mL Schlenk tube was charged with the pentahydrido complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}H)_2$ (30.0 mg, 42.0 μmol), styrene (97.1 μL, 840 μmol), and THF (1.0 mL). Then, the solution was allowed to react for 19 h at 23 °C with vigorous stirring. After the solvent and remaining styrene were removed under reduced pressure, the residual solid was dissolved in THF-d_8. Formation of a μ_3-styrylidene complex **5a** (66.7% yield) with a μ_3-(⊥)-phenylacetylene complex **1a** (33.3% yield) was observed by means of ^{1}H NMR spectroscopy. Complex **1a** was characterized by comparing the spectra with its authentic [9]. ^{1}H NMR (400 MHz, THF-d_8, −30 °C): δ −18.73 (d, $J_{H-H} = 4.6$ Hz, 1H, Ru–*H*), −17.16 (d, $J_{H-H} = 3.9$ Hz, 1H, Ru–*H*), −12.27 (dd, $J_{H-H} = 4.6$, 3.9 Hz, 1 H, Ru–*H*), 1.55 (s, 15H, C_5Me_5), 1.70 (s, 15H, C_5Me_5), 1.79 (s, 15H, C_5Me_5), 5.19 (s, 1H, μ_3-CCPh*H*), 6.85 (t, $J_{H-H} = 7.2$ Hz, 1H, *p-Ph*), 7.01 (t, $J_{H-H} = 7.2$ Hz, 2H, *m-Ph*), 7.29 (d, $J_{H-H} = 7.2$ Hz, 2H, *o-Ph*). ^{13}C NMR (100 MHz, THF-d_8, −30 °C): δ 11.4 (q, $J_{CH} = 126.7$ Hz, C_5Me_5), 12.5 (q, $J_{C-H} = 126.2$ Hz, C_5Me_5), 13.2 (q, $J_{C-H} = 126.4$ Hz, C_5Me_5), 79.7 (d, $J_{C-H} = 155.0$ Hz, μ_3-C═*C*PhH), 90.2 (s, C_5Me_5), 91.5 (s, C_5Me_5), 91.9 (s, C_5Me_5), 123.8 (d, $J_{C-H} = 159.9$ Hz, *Ph*), 127.0 (d, $J_{C-H} = 155.4$ Hz, *Ph*), 128.9 (d, $J_{C-H} = 156.3$ Hz, *Ph*), 147.2 (s, *Ph-ipso*), 324.9 (s, μ_3-*C*═CPhH).

4.11. Thermolysis of the mixture containing **5a** and **1a** at 80 °C

An NMR tube was charged with the pentahydrido complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}H)_2$ (9.0 mg, 12.6 μmol), styrene (12.0 μL, 103.8 μmol, 10 equiv.), C_6D_6 (0.40 mL), and hexamethylbenzene (2.1 mg, 12.6 μmol) as an internal standard. The solution was allowed to react for 19 h at 25 °C. Formation of an equilibrating mixture of **5a** and **1a** with a mole ratio of 2:1 was observed by means of ^{1}H NMR spectroscopy. Then, the solution was heated at 80 °C for 1 h. Quantitative conversion of **5a** into **1a** was monitored by means of ^{1}H NMR spectroscopy.

4.12. ($Cp^*Ru)_3(\mu_3$-C═CHPh)$(H)_3(PMe_3)$ (**6**)

An NMR tube was charged with the pentahydrido complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu\text{-}H)_2$ (16.1 mg, 22.6 μmol), styrene (26.0 μL, 225.0 μmol), C_6D_6 (0.40 mL), and hexamethylbenzene (3.6 mg, 21.5 μmol) as an internal standard. The NMR tube was allowed to react for 24 h at 25 °C. Formation of a μ_3-styrylidene complex **5a** was confirmed by ^{1}H NMR spectroscopy (47.5% yield), and then trimethylphosphine (toluene solution, 2 M, 12.0 μL) was added into the solution. Formation of **6** was observed by ^{1}H NMR spectroscopy (40.9% yield). ^{1}H NMR (400 MHz, toluene-d_8, −50 °C): δ −21.04 (d, $J_{P-H} = 26.8$ Hz, 1H, Ru–*H*), −17.30 (s, 1H, Ru–*H*), −17.16 (d, $J_{P-H} = 47.2$ Hz, 1H, Ru–*H*), 1.32 (d, $J_{P-H} = 8.8$ Hz, 9H, PMe_3), 1.61 (s, d, $J_{P-H} = 1.2$ Hz, 15H, C_5Me_5), 1.64 (s, 15H, C_5Me_5), 2.18 (s, 15H, C_5Me_5), 5.36 (s, 1H, μ_3-C═CPh*H*), 6.82 (t, $J_{H-H} = 6.8$ Hz, 1H, *p-Ph*), 7.32 (d, $J_{H-H} = 6.8$ Hz, 2H, *o-Ph*), 7.69 (t, $J_{H-H} = 8.0$ Hz, 2H, *m-Ph*). ^{13}C NMR (100 MHz, C_6D_6, 23 °C): δ 11.7 (q, $J_{C-H} = 126.6$ Hz, C_5Me_5), 11.8 (q, $J_{C-H} = 126.6$ Hz, C_5Me_5), 13.4 (q, $J_{C-H} = 126.0$ Hz, C_5Me_5), 13.9 (q, $J_{C-H} = 125.5$ Hz, PMe_3), 79.3 (d, $J_{C-H} = 155.3$ Hz, μ_3-C═*C*PhH), 85.9 (s, C_5Me_5), 88.1 (s, C_5Me_5), 94.4 (d, $J_{C-P} = 1.6$ Hz, C_5Me_5), 121.0 (d, $J_{C-H} = 156.4$ Hz, *Ph*), 123.4 (d, $J_{C-H} = 148.7$ Hz, *Ph*), 125.6 (d, $J_{C-H} = 159.2$ Hz, *Ph*), 148.1 (s, *ipso-Ph*), 265.7 (br, $w_{1/2} = 3.2$ Hz, μ_3-*C*═CPhH). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 23 °C): δ −1.4 (s, *P*Me_3).

4.13. Protonation of **2a**

An NMR tube was charged with **2a** (31.6 mg, 35.2 μmol), CD_2Cl_2 (0.45 mL), and cyclooctane (1.0 μL) as an internal standard. Then, $HBF_4{\cdot}Me_2O$ (5.0 μL, 1.2 equiv.) was added to this solution at 23 °C. Formation of ethylbenzene was observed by means of ^{1}H NMR spectroscopy in 5 min (δ 1.22 (t, 2H,$J_{H-H} = 7.2$ Hz, –CH_2–) andδ 2.63 (q, 3H, $J_{H-H} = 7.2$ Hz, –CH_3)). The yield was estimated at 99% on the basis of the integral ratio of the methylene signal of the ethylbenzene with respect to the internal standard. Formation of ethylbenzene was also confirmed by means of gas chromatography by comparing the retention time with that of authentic. Unidentified paramagnetic organometallic compound was also produced by the protonation of **2a**. A broad ^{1}H signal assignable to this compound was observed at δ 22.48 (br, $w_{1/2} = 2271$ Hz).

4.14. Thermolysis of **2a** under argon atmosphere, formation of {$Cp^*Ru(\mu\text{-}CO)\}_3(\mu_3$-$CCH_2Ph)$ (**7a**) and μ_3-methylidyne complex, {$Cp^*Ru(\mu\text{-}CO)\}_3(\mu_3$-CH) (**8**)

An NMR tube was charged with **2a** (25.3 mg, 28.1 μmol), *p*-xylene-d_8 (0.45 mL), and cyclooctane (1.0 μL) as an internal standard. The NMR tube was sealed, and then heated at 120 °C. The reaction was monitored by ^{1}H NMR spectroscopy. Formation of μ_3-phenethylidyne complex **7a**, μ_3-methylidyne complex **8**, and unidentified paramagnetic complex (δ 15.51, br, $w_{1/2} = 511.9$ Hz) were observed with decrease of **2a**. All of **2a** was consumed in 110 h. On the basis of the ^{1}H NMR spectrum measured at this time, the yields of **7a** and **8** were estimated at 5% and 45%, respectively. ^{1}H NMR data for **7a** (400 MHz, C_6D_6, 23 °C): δ 1.57 (s, 45H, C_5Me_5), 6.36 (s, 2H, –CH_2Ph), 7.17 (t, $J_{H-H} = 7.7$ Hz, 1H, *p-Ph*), 7.30 (t, $J_{H-H} = 7.7$ Hz, 2H, *m-Ph*), 7.66 (d, $J_{H-H} = 7.7$ Hz, 2H, *o-Ph*). **8**; ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ 1.73 (s, 45H, C_5Me_5), 14.91 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz,

C_6D_6, 23 °C): δ 9.78 (q, $J_{C-H} = 126.5$ Hz, C_5Me_5), 99.3 (s, C_5Me_5), 247.1 (s, μ-*C*O), 305.6 (d, $J_{C-H} = 161.4$ Hz, μ_3-*C*H). IR (ATR, cm^{-1}): 2983, 2960, 1777, 1734, 1480, 1454, 1430, 1376, 1026, 872, 639.

4.15. Thermolysis of **2a** under CO atmosphere

A 50 mL Schlenk tube was charged with **1a** (42.3 mg, 52.0 μmol) and toluene (3 mL). The reaction solution was frozen by the use of a liquid-nitrogen bath, and then the tube was evacuated. After the tube was warmed up to 25 °C, 1 atm of CO was introduced into the tube. The solution was allowed to react for 18 h at 60 °C with vigorous stirring. The color of solution turned from dark-green to red-brown. Removal of the solvent under reduced pressure afforded a 44.4 mg amount of a mixture of **2a** and **7a**. The ratio between **2a** and **7a** was estimated at 90:10 on the basis of the ^{1}H NMR spectrum of the mixture.

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Appendix A. Supplementary data

The results of VT ^{1}H NMR studies of **2a** and crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 299925–299927. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.070.

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