

BCSJ Award Article

Synthesis, Structures, and Reactions of Coordinatively Unsaturated Trinuclear Ruthenium Polyhydrido Complexes, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](Y)$ ($Y = BF_4$, CF_3SO_3, $1/2(SO_4)$, $C_6H_5CO_2$, CH_3CO_2, $B(C_6H_5)_4$, PF_6) and $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$

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Cationic triruthenium hexahydrido complexes, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](Y)$ ($Y = BF_4$, CF_3SO_3, $1/2(SO_4)$, $C_6H_5CO_2$, CH_3CO_2), have been synthesized by the reaction of diruthenium tetrahydride $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]$ with the corresponding acid, HBF_4, CF_3CO_2H, H_2SO_4, $C_6H_5CO_2H$, and CH_3CO_2H. The trimeric structure of these complexes has been confirmed by a crystallographic study of $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](PF_6)$. The treatment of $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](Y)$ with CH_3ONa in methanol selectively afforded a neutral trinuclear pentahydrido complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$, which underwent an intermolecular H/D exchange reaction with benzene-d_6, toluene-d_8, or *o*-xylene-d_{10} to give $[\{Ru(C_5Me_5)\}_3(\mu\text{-}D)_3(\mu_3\text{-}D)_2]$ as the result of arene C–H bond activation via an η^2-arene intermediate complex. A cationic hydrido complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](Y)$, having a carboxylate as a counter anion was equilibrated with $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ in solution, and the equilibrium constant depended on the counter anion. An X-ray diffraction study showed that $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ has a triangular reaction field surrounded by three C_5Me_5 ligands. The reaction of $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ with 1 equiv of O_2 proceeded with the retention of the Ru_3 framework to yield an 80/20 mixture of a mono-μ_3-oxo complex $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}O)]$ and a di-μ_3-oxo complex $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}O)_2]$. A novel trinuclear μ_3-iodo-tetra-μ-hydrido complex, $[\{Ru(C_5Me_5)\}_3(\mu_3\text{-}H)(\mu\text{-}H)_3(\mu_3\text{-}I)]$ was formed upon the treatment of $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ with 1 equiv of CH_3I in tetrahydrofuran. The treatment of $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ with carbon monoxide generated a paramagnetic trinuclear tetracarbonyl complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$.

The reactivity of transition metal cluster complexes has been of special interest in the area of recent organometallic chemistry in anticipation of their remarkable reactivity due to the synergy of adjacent metal centers. In a multimetallic reaction site of the cluster complex, substrates are often effectively activated in a manner different from that achieved by a mononuclear complex. This is most probably due to a cooperative action of the metal centers. A large number of studies on the reaction chemistry of clusters have thus far been reported.[1] However, most of the metal clusters used in these studies have been carbonylmetal complexes, or clusters directly derived from them. In contrast to metal carbonyl clusters, metal polyhydrido clusters have thus far been relatively unexplored, probably due to their instability, and the lack of a rational synthetic method applicable to the many ligand/metal combinations, although they are expected to be much more active than the polycarbonyl clusters in the oxidative addition of the substrates.

Among the intrinsic properties of metal clusters, their capability for multiple-coordination is probably the most essential point concerning the multimetallic activation, namely, multiple-coordination seems likely to be an origin of the "cluster effect" and should give rise to cooperation of the metal centers in the activation of the substrate. Therefore, we adopted a metal polyhydrido cluster, especially a cluster having bridging hydrido ligands, as a precursor of the active species for multime-

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tallic activation. The liberation of bridging hydrido ligands from the cluster generates, spontaneously, multiple vacant coordination sites on the adjacent metal centers, all together.

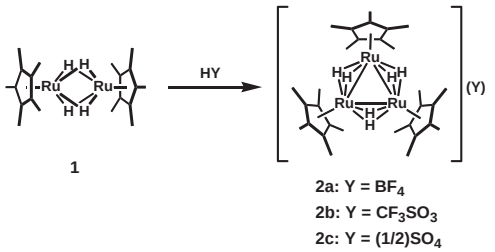
Although there have, thus far, been several reported examples of multinuclear polyhydrido-bridged complexes,[2–16] their reaction chemistry is not as remarkable or unique, unfortunately.

As a part of our early efforts directed toward preparing the polynuclear polyhydrido complexes, we reported on the synthesis and reactions of a dinuclear tetrahydrido-bridged complex of ruthenium, $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]$ (**1**), and demonstrated several typical examples of bimetallic activation by using **1** as a precursor of the active species.[17–31]

Here, we describe in full detail the synthesis, characterization, and some reactions of trinuclear ruthenium polyhydrido complexes, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](Y)$ ($Y = BF_4$, CF_3SO_3, $1/2(SO_4)$, $C_6H_5CO_2$, CH_3CO_2, BPh_4, and PF_6) and $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$.

Results and Discussion

Synthesis of Cationic Triruthenium Hexahydrido Complexes, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](Y)$ ($Y = BF_4$, CF_3SO_3, $1/2(SO_4)$, $C_6H_5CO_2$, CH_3CO_2, BPh_4, and PF_6). The addition of an equimolar amount of $HBF_4 \cdot OEt_2$ to a suspension of a diruthenium tetrahydrido complex, $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]$ (**1**), in tetrahydrofuran gave a cationic trinuclear hydrido complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](BF_4)$ (**2a**), in excellent yield (Eq. 1).



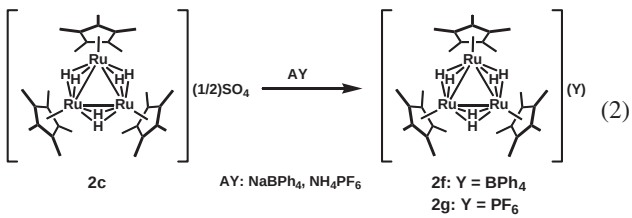
(1)

Although the protonation of **1** proceeded very slowly below 0 °C, a mixture of a red suspension of the starting hydrido complex **1** and the acid gradually turned brown-purple with the evolution of dihydrogen upon warming to room temperature. A workup gave **2a** as a purple microcrystalline solid in 88% yield. When $HBF_4 \cdot OEt_2$ was added to **1** at room temperature, the reaction completed instantly with vigorous evolution of dihydrogen, resulting in a quantitative formation of **2a**.

Analogous procedures using acids having a non-coordinating, less-nucleophilic conjugate base led to the corresponding cationic trinuclear hexahydrido complexes **2**. For example, the reaction of **1** with excess CF_3SO_3H smoothly proceeded to give the corresponding cationic complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](CF_3SO_3)$ (**2b**). In contrast to these reactions, the use of sulfuric acid brought about a somewhat complicated result. When compound **1** was treated with an equimolar amoumt of H_2SO_4, a purple-brown solid of a cationic complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](1/2SO_4 + H_2SO_4)$ (**2c**), was formed, in which excess H_2SO_4 was incorporated into the product through a hydrogen bond to the sulfate ion. The incorporation of H_2SO_4 was confirmed by means of ^1H NMR and IR spectroscopy. The ^1H NMR spectrum of **2c** recorded in $CDCl_3$ at room temperature revealed a broad resonance signal around δ 5.9 (2H) of H_2SO_4, incorporated into the molecule together with those of C_5Me_5 (δ 2.00, 45H) and hydrido (δ −11.23, 6H) ligands. A strong and broad absorption for the O–H stretching vibration of H_2SO_4 with a hydrogen-bonding interaction appeared in the range of 3000–3500 cm^{-1} in the IR spectrum. The amount of sulfuric acid incorporated in **2c** changed over a wide range along with a change in the amount of acid used in the reaction. However, excess sulfuric acid incorporated in **2c** could hardly be removed, despite evacuation or washing with diethyl ether.

The reaction of **1** with an acid having a nucleophilic conjugate base caused a more complicated result. The reaction of **1** with carboxylic acid, such as benzoic acid or acetic acid, yielded the corresponding cationic hexahydrido complex, **2d** ($Y = C_6H_5CO_2$) or **2e** ($Y = CH_3CO_2$), respectively, together with a dinuclear di-μ-carboxylato complex, **3d** or **3e** (vide infra).[32]

Trinuclear hexahydrido complexes **2a–c** are stable in solution, even in chloroform, at room temperature, and can be kept in chloroform for several hours without decomposition, while **2d** and **2e** are labile in solution. Since single crystals suitable for X-ray diffraction could not be obtained by the recrystallization of **2a–c** from tetrahydrofuran, an exchange of the counter anion was attempted. The counter anion of the cationic complex **2c**, $1/2SO_4^-$, was readily replaced by BPh_4^- or PF_6^- upon a treatment with $NaBPh_4$ or NH_4PF_6. The addition of an excess amount of $NaBPh_4$ or NH_4PF_6 to a suspension of **2c** in tetrahydrofuran gave the corresponding cationic complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](Y)$ ($Y = BPh_4$ (**2f**) or PF_6 (**2g**)), in good yield (Eq. 2).



(2)

Complexes **2f** and **2g** are stable both in the solid state and in solution. Single crystals of **2f** and **2g** suitable for X-ray diffraction studies were obtained from tetrahydrofuran and 1,2-dimethoxyethane, respectively.

The cationic hexahydrido complexes **2a–g** were characterized based on the ^1H and ^{13}C NMR and IR spectroscopies, as well as the electric conductivity. While cationic hydrido complexes, **2d** and **2e**, immediately decomposed in chloroform-d_3, they remained unchanged for at least several minutes in dichloromethane. Their NMR spectra were, therefore, recorded in dichloromethane-d_2.

In the ^1H NMR spectra of hexahydrido complexes **2a–g**, a signal of the hydrido ligands appeared at around δ −11.2 as a singlet peak. A variable-temperature ^1H NMR measurement of **2a** in acetone-d_6 showed that the signals of the C_5Me_5 groups and the hydrido ligands were observed as a singlet peak, respectively, in the temperature range from 50 °C to −90 °C. The half-height width of the signal of the hydrido ligands slightly broadened upon lowering the temperature from 2.2 Hz (at 50 °C) to 4.0 Hz (−90 °C). This result implied that

the cationic hexahydrido complex has a pseudo-threefold symmetry axis; also the six hydrido ligands were observed to be indistinguishable. A structure having two sets of three identical hydrides, namely, three bridging hydrides and three terminal hydrides, cannot be ruled out altogether, if they rapidly exchange each coordination site within the NMR time-scale. A structure having six bridging hydrides was, however, supported by an ab initio calculation,[33] and was confirmed by an X-ray diffraction study of **2g** (vide infra).

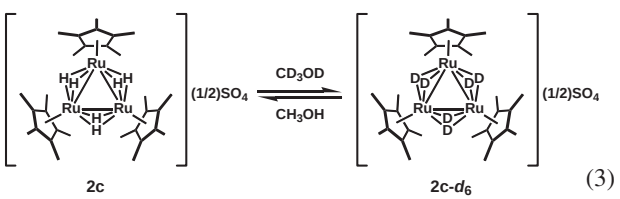
In order to clarify the bonding mode of the hydrido ligands in **2a**, η^2-H_2 or η^1-H, we measured the relaxation time (T_1) by using standard JEOL programs. The T_1 values for the resonance signal at δ −11.23, measured in CD_2Cl_2 at 500 MHz, were found to be 385 ms (at −50 °C) and 387 ms (at −80 °C). These values are larger than that of the hydride signal in the dihydrogen complexes, and lies within the range of those for the classical hydrido complexes.[34] Consequently, we concluded that not only **2a**, but also a series of the cationic triruthenium hexahydrido complexes **2**, are the classical hydrido complexes. This result is consistent with the relatively long distance between the two hydrogen atoms bridging the same Ru–Ru bond observed in the X-ray structure of **2g** (vide infra).

The cationic complex **2b** was alternatively prepared by the treatment of **1** with an ester, $CF_3SO_3CH_3$, instead of the acid, CF_3SO_3H. In this case, as anticipated, the formation of **2b** was accompanied by the evolution of methane.

Whereas the reaction conducted in tetrahydrofuran generated the cationic complex **2**, the reaction in the presence of CH_3CN or benzene yielded a cationic mononuclear coordinatively saturated complex, $[Ru(C_5Me_5)(CH_3CN)_3](Y)$[35] or $[Ru(C_5Me_5)(C_6H_6)](Y)$,[17,23] respectively.

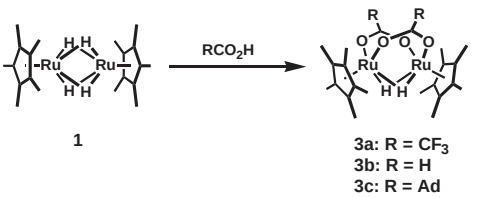
An ethyltetramethylcyclopentadienyl analogue, $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)_6]1/2(SO_4 + H_2SO_4)$ (**2c′**), was obtained in excellent yield in the reaction of $[\{Ru(C_5Me_4Et)\}_2(\mu\text{-}H)_4]$[36] with sulfuric acid, and the sulfate ion of **2c′** was readily exchanged with BPh_4^- to form $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)_6](BPh_4)$ (**2f′**) by a treatment of **2c′** with $NaBPh_4$ in tetrahydrofuran.

Hydrido ligands that exhibit an acidic character in polar solvents can readily undergo an intermolecular hydrogen exchange reaction with a protic solvent, such as alcohol. An exchange of the hydrido ligands in **2** with methanol was examined by means of an isotopic labeling experiment using a deuterated solvent. Monitoring the H/D exchange reaction between **2c** and methanol-d_4 by ^{1}H NMR spectroscopy showed that the reaction did not take place at room temperature, but was completed upon heating at 80 °C for 4 h. The half-height width of the hydrido signal significantly broadened with the progress of the exchange reaction. This process is, of course, reversible and the starting hexahydrido complex **2c** is quantitatively recovered when **2c**-d_6 is heated in methanol-h_4 at 80 °C for 4 h (Eq. 3).

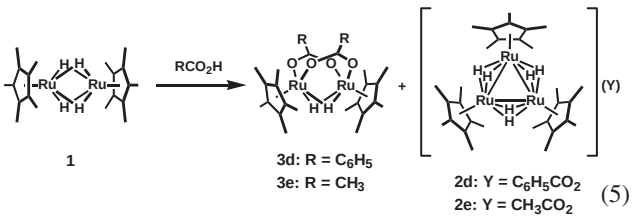


(3)

Synthesis and Structure Determination of the Di-μ-carboxylato-di-μ-hydrido-bis[(pentamethyl-η^5-cyclopentadienyl)ruthenium], $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}OCOR)_2]$ (R = CF_3, H, and Adamantyl). As mentioned above, an acid bearing a bulky and less-nucleophilic conjugate base, such as HBF_4 and CH_3SO_3H, reacts with **1** to form the cationic trinuclear hexahydrido complex **2**. The reaction of **1** with a series of carboxylic acids, however, leads to the formation of neutral dinuclear di-μ-carboxylato complexes **3**, as the result of a nucleophilic attack of the carboxylato anion at the cationic metal centers of an intermediary dicationic diruthenium species, $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]^{2+}$ (vide infra). The treatment of **1** with excess carboxylic acid, such as CF_3CO_2H, HCO_2H, or $AdCO_2H$ (Ad = adamantyl), in tetrahydrofuran exclusively gave a neutral dinuclear di-μ-carboxylato-di-μ-hydrido complex, $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}OCOR)_2]$ (R = CF_3 (**3a**), H (**3b**), and Ad (**3c**)), in excellent yields along with the release of H_2 (Eq. 4).[32] Benzoic acid or acetic acid, however, produced a moderate result between those brought about by mineral acids, such as HBF_4 or H_2SO_4, and carboxylic acid, such as trifluoroacetic acid, formic acid, and 1-adamantanecarboxylic acid. The reaction of **1** with excess benzoic acid or acetic acid gave a mixture of the corresponding di-μ-carboxylato-di-μ-hydrido complex **3** (R = C_6H_5 (**3d**) and CH_3 (**3e**)) and the cationic hexahydrido complex **2** (Eq. 5). The product distribution between two hydrido complexes **3**/**2** was about 3/1 in each case.



(4)



(5)

The di-μ-carboxylato-di-μ-hydrido complexes **3** are stable in the solid state and are very soluble in diethyl ether or toluene, whereas the cationic complex **2** is sparingly soluble in such less-polar solvents. Complexes **2** and **3** formed in the reaction could, therefore, be readily separated from each other by extraction with diethyl ether.

Complexes **3a**–**3e** were characterized on the basis of ^{1}H, ^{13}C, and ^{19}F NMR and infrared spectra. In the ^{1}H NMR spectra, a singlet resonance signal of intensity 2H for the bridging hydrides appeared in the range of δ −4.50 to −4.10 ppm, which is significantly low field compared to those for the hydrido ligands in the dinuclear tetrahydride **1** (δ −13.99 in C_6D_6)[17,23] or the cationic trinuclear complexes **2** (δ ca. −11.2). The longitudinal relaxation time (T_1) for the hydrido ligands in **3a** was determined to be 251 ms at −50 °C by using the inversion–recovery method. The observed T_1 value is sufficient to characterize the complex as a classical dihydrido complex.

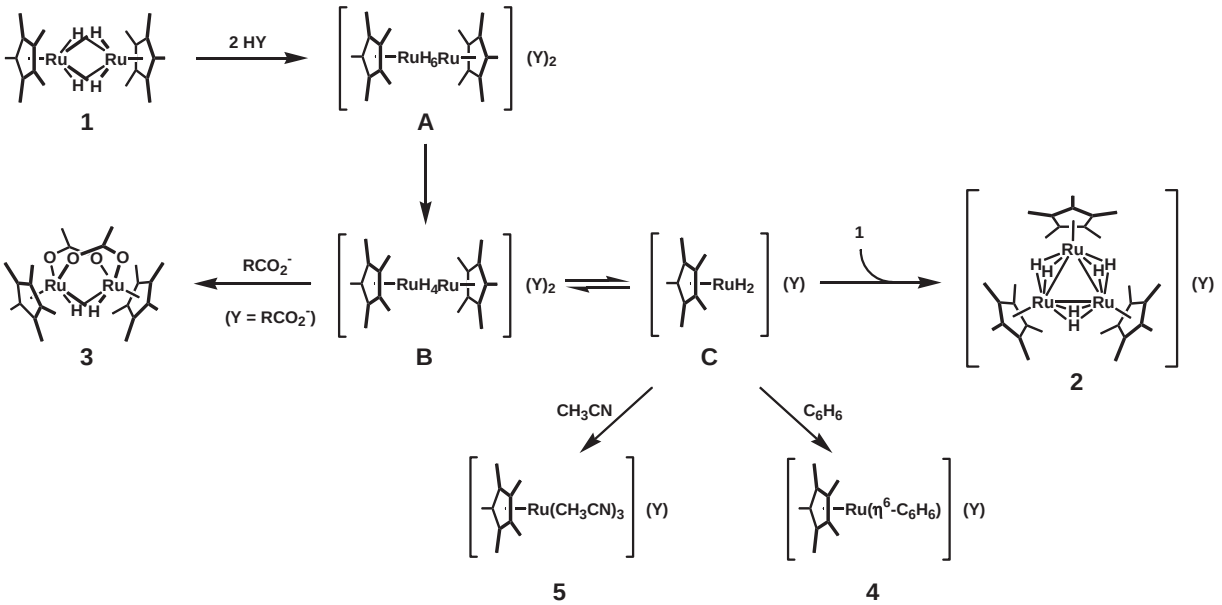
The two C_5Me_5 groups were observed to be equivalent, as demonstrated by the presence of a singlet peak of intensity 30H in the δ 1.70 to 1.84 region. There is evidently a symmetry element that relates the two ruthenium atoms; most likely, this is a mirror plane that bisects the ruthenium–ruthenium vector and passes through the two bridging hydrides and the two acetoxy carbon atoms. The infrared spectra of complexes **3** revealed strong absorption bands characteristic of a bidentate carboxylato ligand in the 1660 to 1560 cm^{-1} region.[38]

The molecular structure of **3a** was confirmed based on an X-ray diffraction study.[39] The structure is fully consistent with the spectral data mentioned above. The two ruthenium atoms are quadruply bridged by the two carboxylato ligands and the two hydrides. The interatomic distances of the two ruthenium atoms is 2.846(2) Å, comparable to that observed in the analogous dinuclear μ-carboxylato complexes, $[\{Ru(C_6H_6)\}_2(\mu\text{-H})(\mu\text{-OH})(\mu\text{-OCOCH}_3)](ClO_4)$ (2.785 Å) and $[\{Ru(C_6H_6)\}_2(\mu\text{-H})_2\{\mu\text{-OCOPh(OH)}\}](ClO_4)$ (2.674 Å).[40] The EAN rule applied to the di-μ-carboxylato-di-μ-hydridodiruthenium **3** requires a metal–metal σ bond between the two ruthenium atoms; this is clearly reflected in the above-mentioned Ru–Ru bond length.

Formation Mechanism of the Cationic Hexahydridotriruthenium 2 and the Di-μ-carboxylato-di-μ-hydridodiruthenium 3. The formation of the trinuclear cationic hexahydrido complex **2** would be reasonably elucidated by the reaction sequence illustrated in Scheme 1.

At the initial stage of the reaction, two protons successively attack the ruthenium centers of **1** to yield a dinuclear dicationic hexahydrido species **A** (30e), which would undergo a reductive elimination of dihydrogen to generate an intermediary highly unsaturated dinuclear dicationic tetrahydride complex **B** (28e). This *protonation–H_2 liberation* step is rationalized by a calculation performed by Morokuma and Koga.[41] Shortening of the interatomic distance between the two adjacent hydrido ligands in the hexahydrido species **A** in comparison to **1** is responsible for giving rise to a bonding interaction between them. The liberation of the dihydrogen was confirmed when the reaction of **1** with an equimolar amount of H_2SO_4 in tetrahydrofuran-d_8 at 10 °C was monitored by means of ^1H NMR spectroscopy. A resonance signal of the liberated dihydrogen appeared at δ 4.54 as a sharp singlet peak, although the integral intensity of the signal was somewhat weak because of its poor solubility in tetrahydrofuran-d_8. The chemical shift of δ 4.54 agreed well with that of dihydrogen saturated in tetrahydrofuran-d_8, and is also fully consistent with that reported for free H_2 liberated from $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ (δ 4.72).[42] In solution, the dicationic species **B** must be in equilibrium with a highly unsaturated mononuclear cationic species **C** (14e), which immediately reacts with the unprotonated dinuclear tetrahydrido complex **1** to form the monocationic trinuclear hexahydrido complex **2**. The reaction of **1** with **C** would be much faster than that of **1** with the dinuclear species **B**, due to sterical reasons. The formation of the trinuclear monocationic complex **2** is, as a result, predominant over that of a tetranuclear dicationic complex resulting from the reaction of **1** with **B**.[43] In fact, the tetranuclear dicationic complex was not detected at all under these conditions. The generation of the intermediate mononuclear cationic species **C** is supported by the fact that treatment of **1** with CF_3SO_3H in benzene quantitatively affords a coordinatively saturated cationic mononuclear complex having an η^6-C_6H_6 ligand, $[Ru(C_5Me_5)(C_6H_6)](CF_3SO_3)$ (**4**),[17,23,35] as a result of the coordinative addition of benzene to **C**, followed by elimination of the two hydrido ligands as a molecular hydrogen. The mononuclear cation **C** was also quenched by acetonitrile molecules to lead to a known cationic complex, $[Ru(C_5Me_5)(CH_3CN)_3](BF_4)$ (**5**),[35] when **1** was treated with $HBF_4 \cdot (OEt_2)$ in diethyl ether in the presence of a large excess amount of acetonitrile.

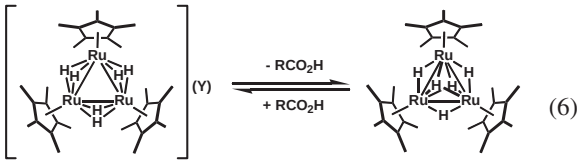
In this mechanism, the dinuclear dicationic species **B** would be captured by the counter anion in the case that the counter anion is less bulky and sufficiently nucleophilic. In the reaction of **1** with carboxylic acid, di-μ-carboxylato complex **3** is predominantly formed due to a nucleophilic attack of the carbox-



Scheme 1.

ylato anion at the metal centers, whereas the reaction of **1** with an acid with a noncoordinating, a less nucleophilic anion, such as HBF_4, CF_3SO_3H, or H_2SO_4, exclusively yields **2**. These facts are also reasonably explicable according to this mechanism.

Synthesis of a Neutral Pentahydridotriruthenium Cluster, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$. The stability of the cationic hexahydrido complexes **2** depends on the counter anions. Complexes **2d** ($Y = C_6H_5CO_2^-$) and **2e** ($Y = CH_3CO_2^-$) are labile in both solid state and solution, while **2a** ($Y = BF_4^-$) and **2b** ($Y = CF_3SO_3^-$) are insensitive toward air and moisture, and do not decompose even in solution at ambient temperature. The decomposition process of **2e** in solution was elucidated by means of ^{1}H NMR spectroscopy. When **2e** was dissolved in benzene-d_6 or tetrahydrofuran-d_8 and allowed to stand at ambient temperature, it decomposed within several minutes to result in the quantitative formation of a neutral trinuclear pentahydrido complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ (**6**). Compound **6** was isolated as a brown-black crystalline solid when the solvent was removed under reduced pressure from the resultant solution. On the contrary, the addition of excess acetic acid to a tetrahydrofuran solution of isolated **6** resulted in a quantitative regeneration of **2e**. These results show that **2e** and **6** are equilibrated in solution (Eq. 6).

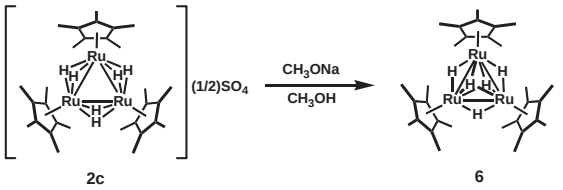


2d: Y = $C_6H_5CO_2$
2e: Y = CH_3CO_2 **6** (6)

The equilibrium process between **2d** and **6** in solution was confirmed in a similar way. The equilibrium constant K, where $K = [\mathbf{2d}]/([\mathbf{6}][C_6H_5CO_2H])$, can be estimated directly based on the ^{1}H NMR integration of the two separate hydride resonance signals of **2d** and **6** observed at δ −11.26 and −7.22, respectively. The results show that the equilibrium constant (K) changes from 0.76 [M^{-1}] at 293 K to 0.14 [M^{-1}] at 333 K. A least-squares fit to the equation $RT \ln K = -\Delta H/T + \Delta S$ shows that $\Delta H = -7.5 \pm 0.3$ kcal mol^{-1} and $\Delta S = -26.5 \pm 1.0$ cal mol^{-1} K^{-1} for the protonation of **6** with benzoic acid to form **2d**.

If an appropriate basic reagent is added to the equilibrated mixture of **2** and **6**, the acid generated in the solution can be trapped. As a result, the equilibrium shifts to the right hand, and a neutral trinuclear pentahydrido complex, **6**, must therefore be obtained in a reasonable yield.

Compound **2c** seems to be the most versatile starting material for the synthesis of **6**, because **2c** can be obtained in excellent yield with simple procedures, and is remarkably stable. Among the reactions of **2c** with various basic reagents, the best result was obtained in a reaction with CH_3ONa. The treatment of **2c** with excess CH_3ONa in methanol at room temperature for 10 min, followed by a chromatographic workup, afforded **6** in 96% yield as a black-brown microcrystalline solid (Eq. 7).



2c **6** (7)

The ethyltetramethylcyclopentadienyl analogue of **6**, $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ (**6′**), was derived from the corresponding cationic hexahydrido complex, $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)_6](BPh_4)$ (**2f′**), in a similar manner.

Compound **6** is soluble in tetrahydrofuran, benzene, and toluene, and is less soluble in diethyl ether, pentane, and hexane. Although **6** is fairly stable in the solid state, even in air, it is extremely sensitive towards oxygen in solution. When a solution of **6** was exposed to atmospheric oxygen at ambient temperature, mono- and dioxygenated products, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}O)]$ (**9**) and $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)(\mu_3\text{-}O)_2]$ (**10**), were consecutively formed within a few seconds (vide infra).

The ^{1}H NMR spectra of **6**, measured in C_6D_6 at room temperature, exhibits two sharp singlet peaks at δ 2.04 and −7.22 for the three C_5Me_5 groups and the five hydrido ligands, respectively. The ^{1}H NMR spectrum is temperature-independent in the temperature range from −120 °C to room temperature. A variable-temperature ^{1}H NMR analysis of **6** in tetrahydrofuran-d_8/toluene-d_8 (5/1) performed at 500 MHz proved that resonances for five hydrido ligands were observed to be equivalent in the temperature range from 20 to −120 °C. The line shape and intensity of the signal assignable to the hydrido ligands remained unchanged over this temperature range, although the signal shifted downfield from δ −7.55 at 20 °C to δ −6.37 at −120 °C. This is probably due to a rapid exchange of the hydrides among the coordination sites, μ_2- and μ_3-sites, on an NMR timescale. The species in which the triply bridging hydride has a bonding interaction with the doubly bridging hydride is one of the possible intermediates or transition states of this dynamic process. Two hydrides would change the coordination sites with each other via rotation around the coordination bond between the resulting η^2-H_2 ligand and the ruthenium center. Site exchange of the hydrido ligands via an intermediary η^2-H_2 complex is proposed for the mononuclear polyhydrido complex.[44–50]

In order to obtain information on the bonding mode of the hydrido ligands in **6**, the relaxation time (T_1) was measured in tetrahydrofuran-d_8 at 500 MHz. The T_1 values of 4.33 s (at −50 °C) and 2.55 s (at −80 °C) for the hydride signal of **6** are significantly large compared with that of the hydride signal of **2a**. Elongation of the relaxation time indicates that there is no bonding interaction among the hydrido ligands in **6**. Complex **6** was, therefore, concluded to be a classical hydrido complex, as well as **2**. A lack of the bonding interaction among the hydrido ligands in **6** is entirely consistent with the long H–H separation determined by an X-ray diffraction study (vide infra).

As anticipated from the equilibrium between **2e** and **6** (Eq. 6), the treatment of **6** with an acid, such as HBF_4, CF_3SO_3H, H_2SO_4, or HPF_6, generates the corresponding cationic hexahydrido complex **2** in a quantitative yield (Eq. 8).

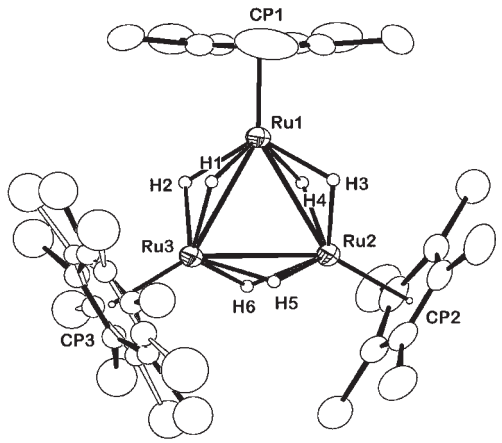
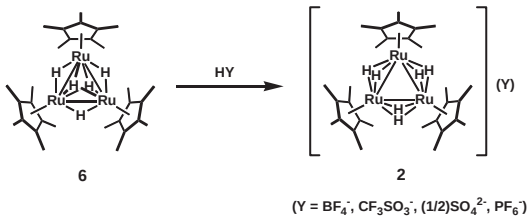


Fig. 1. Thermal ellipsoid representation of [{Ru(C_5Me_5)-(μ-H)$_2$}$_3$](PF_6) (**2g**) showing 30% probability ellipsoids. The anion, PF_6, and dioxane molecules are omitted for clarity. CP is centroid of the C_5Me_5 ring.

Table 1. Selected Bond Distances (Å) and Angles (deg) in [{Ru(C_5Me_5)(μ-H)$_2$}$_3$](PF_6) (**2g**)

	Bond distances		
Ru1–Ru2	2.7033(8)	Ru1–CP1	1.836
Ru1–Ru3	2.7078(10)	Ru2–CP2	1.851
Ru2–Ru3	2.7079(11)	Ru3–CP3	1.836
Ru–H	1.71 (av)		
	Angles		
Ru1–Ru2–Ru3	60.06(3)	Ru2–Ru3–Ru1	59.89(2)
Ru3–Ru1–Ru2	60.05(2)		



(8)

X-ray Crystal Structures of [{Ru(C_5Me_5)}$_3$(μ-H)$_6$](PF_6) (2g) and [{Ru(C_5Me_5)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6). Single crystals of **2a** and **2f** with reasonable size were obtained from tetrahydrofuran at −20 °C. However, we could not collect diffraction data with sufficient quality because of a loss of the solvent molecules included in the crystal during data collection. After several attempts to crystallize **2a**, **2f**, and **2g** from solvents with higher boiling points, we successfully obtained single crystals of **2g** suitable for an X-ray structural characterization from the mixed solvent of dioxane and 1,2-dimethoxyethane (1/1) at 5 °C. Data collection and refinement proceeded without problems; the refinement converged with residuals of $R_1 = 0.045$ ($wR_2 = 0.118$). In a unit cell, two cations [{Ru(C_5Me_5)}$_3$(μ-H)$_6$]$^+$, two counter anions, PF_6^-, and six dioxane molecules are included. Hydrogen atoms bonded to the ruthenium atoms were located by a difference Fourier synthesis, and were refined isotropically. The structure of the cationic part of **2g** is shown in Fig. 1. The counter anions and dioxane molecules are disregarded for clarity. Selected intramolecular distances and angles are listed in Table 1. Compound **2g** consists of a nearly equilateral triangular cluster of the three ruthenium atoms with the six doubly bridging hydrido ligands. Each Ru–Ru bond is bridged by the two hydrogen atoms; one of them is up and the other is down with respect to the Ru_3 plane. The separation of the two hydrogen atoms bridging the same Ru–Ru bond, av. 1.74 Å, is larger than the H–H distance reported for the dihydrogen ligands (ca. 0.8–1.05 Å)[51] in the mononuclear complexes; this clearly shows that **2g** is a classical hydrido complex. The average Ru–Ru distance of 2.7063(10) Å is somewhat shorter than that reported for the Ru–Ru single bond. The EAN rule applied to **2g** requires a formal Ru–Ru bond order of 5/3. Shortening of the Ru–Ru bond is most likely due to the two three-center, two-electron Ru–H–Ru bonds.

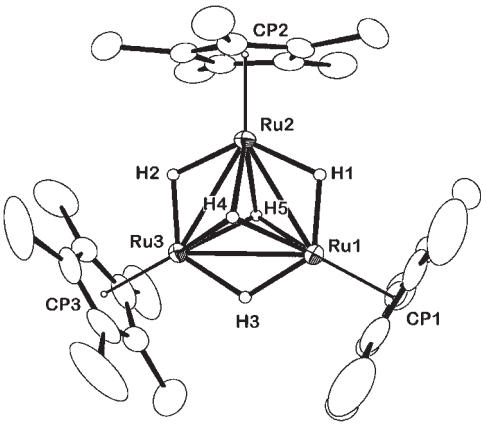


Fig. 2. Thermal ellipsoid representation of [{Ru(C_5Me_5)}$_3$-(μ-H)$_3$(μ_3-H)$_2$] (**6**) showing 30% probability ellipsoids. CP is centroid of the C_5Me_5 ring.

Table 2. Selected Bond Distances (Å) and Angles (deg) in [{Ru(C_5Me_5)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (**6**)

	Bond distances		
Ru1–Ru2	2.7534(8)	Ru1–CP1	1.808
Ru1–Ru3	2.7503(8)	Ru2–CP2	1.811
Ru2–Ru3	2.7453(6)	Ru3–CP3	1.808
Ru–μ-H	1.66 (av)	Ru–μ_3-H	1.94 (av)
	Angles		
Ru1–Ru2–Ru3	60.02(2)	Ru2–Ru3–Ru1	60.135(18)
Ru3–Ru1–Ru2	59.844(18)		

The structure of the neutral cluster **6** was determined by X-ray crystallography using a dark-brown prismatic single crystal that was obtained from a 4:1 mixed solvent of tetrahydrofuran and pentane at −20 °C. Diffraction data were collected at −55 °C. The positions of the hydrogen atoms directly bonded to the ruthenium atoms were located by a sequential difference Fourier synthesis, but were not refined. Figure 2 displays the molecular structure of **6**, and Table 2 lists the selected bond distances and angles. The structure of **6** is approximately in the C_{3v} symmetry, except for the array of C_5Me_5 rings. Three doubly bridging hydrogen atoms and two triply bridging ones bond three ruthenium atoms, which occupy the vertices of a nearly equilateral triangle. The average interatomic distance between the μ_3-H and μ-H atoms in **6** is 2.07 Å, which is larger than

the value (av. 1.74 Å) for the two hydrogen atoms bridging the same Ru–Ru bond in **2g**. This fact shows that there is no bonding interaction among the hydrido ligands, and that **6** is a typical classical hydrido complex. The average Ru–Ru distance of 2.7497(7) Å is significantly longer than that observed in the cationic hexahydrido complex **2g**, although both **6** and **2g** are 44-electron complexes. This is probably due to the difference in the numbers of the bridging hydrides, two μ_3-hydrogens and three μ-hydrogens in **6** vs six μ-hydrogens in **2g**. The ruthenium centers in **2g** are, therefore, bound to each other more tightly than those in **6**. The average distance between Ru and the centroid of the C_5Me_5 ring is 1.809 Å, and slightly shorter than that observed in **2g** (1.841 Å). The difference in the electron density at the metal centers between **6** and **2g** is most probably responsible for the difference in the Ru–centroid distance. Lowering the electron density at the metal center in cationic **2g** reduces back-donation from the ruthenium to the C_5Me_5 group and, as a result, the Ru–centroid distance in **2g** is lengthened compared to that in the neutral complex **6**.

H/D Exchange Reaction of 6 with Benzene-d_6, Toluene-d_8, *o*-Xylene-d_{10}, and D_2. The hydrido ligands of **6** undergo an intermolecular exchange reaction with hydrogen atoms attached to aromatic rings. A solution of pentahydride **6** in C_6D_6 (0.014 M) was heated in a sealed NMR sample tube at 80 °C, and the H/D exchange reaction was monitored by means of ^{1}H NMR spectroscopy. Upon heating for 5 h, five resonance signals assignable to hydrides for the isotopomers **6**-d_0, **6**-d_1, **6**-d_2, **6**-d_3, and **6**-d_4 appeared at δ −7.26, −7.85, −8.47, −9.09, and −9.72, respectively. After an additional heating for 17 h, 61% of the hydrido ligands were converted into the deuteride, and the molar ratio of the isotopomers **6**-d_0/**6**-d_1/**6**-d_2/**6**-d_3/**6**-d_4/**6**-d_5 became 2/9/23/31/21/14 (Fig. 3-B). After 40 h, the ratio reached 0/3/12/28/32/25 at 73% conversion (Fig. 3-C).

As the reaction proceeded, a progressive increase in the integral intensity of the ^{1}H signals in the aromatic region was observed. Within the period of monitoring the reaction, the formation of any product other than **6**-d_n (n = 1–5) was not observed. Based on these observations, we can propose a couple of plausible reaction paths involving an intermediary η^2:η^2:η^2-C_6D_6 or η^2-C_6D_6 complex. Previously, we reported that the pentahydride **6** reacted with 1,3- or 1,4-cyclohexadiene to form a trinuclear μ_3-η^2:η^2:η^2-C_6H_6 complex **7** via an allylic C–H bond activation, followed by β-H elimination (Scheme 2).[52]

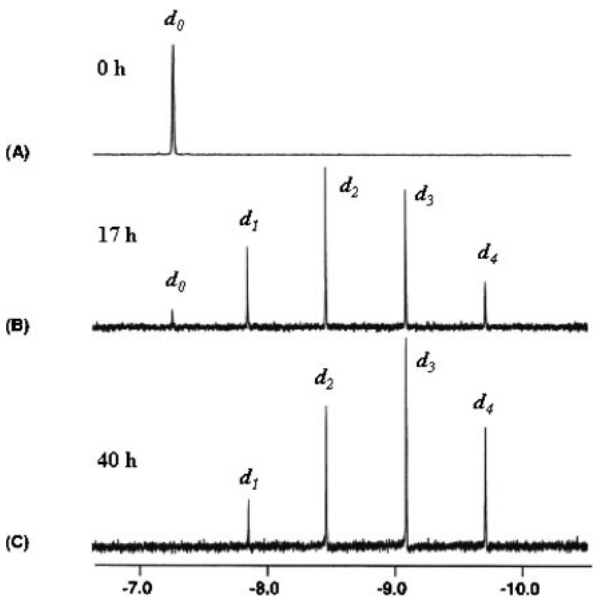
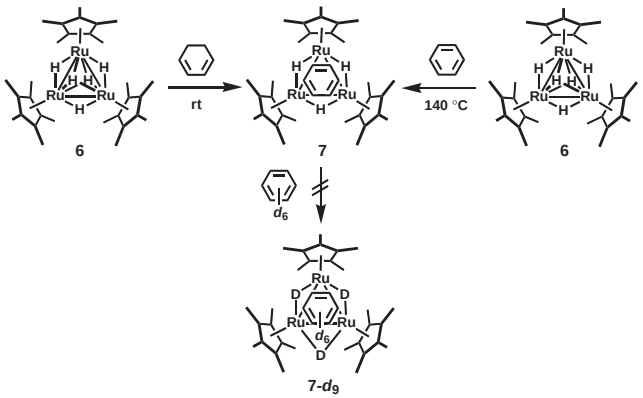


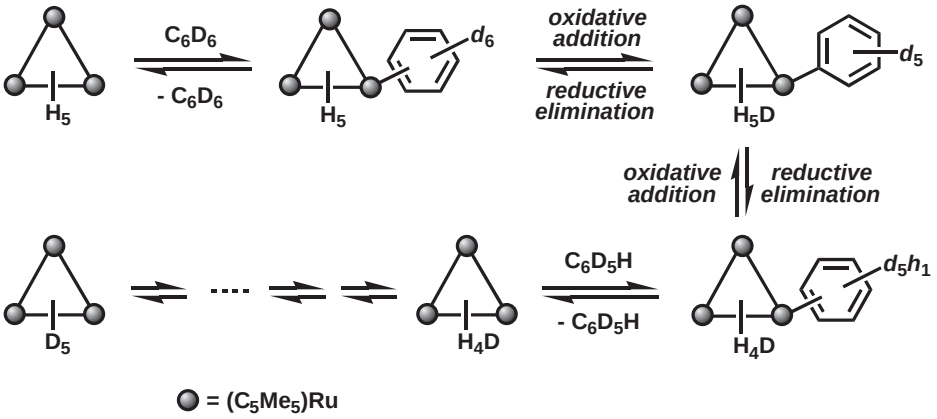
Fig. 3. ^{1}H NMR spectra of the hydride regions in the H/D exchange reaction of **6** with C_6D_6 at 80 °C.



Scheme 2.

The face-capping benzene complex **7** was alternatively obtained by heating the pentahydride **6** in benzene at 140 °C for 17 h. The benzene ligand in **7** is tightly bound to the metal centers, and added benzene-d_6 could not replace the coordinated benzene-h_6 to generate **7**-d_6 when isolated **7**-h_6 was heated at 140 °C in C_6D_6 for 68 h. More noteworthy is that the hydrogen atoms in neither the C_6H_6 ligand nor the hydrido ligands in **7** were exchanged with deuterium in C_6D_6 under these conditions. As mentioned above, the H/D exchange between **6** and C_6D_6 was realized under much milder conditions than those which brought about the incorporation of a benzene molecule in the Ru_3 core of **6**. These results altogether rule out the possibility that the H/D exchange between the hydrides in **6** and C_6D_6 proceeds via an intermediate μ_3-η^2:η^2:η^2-C_6D_6 complex **7**. Another plausible path for the H/D exchange reaction is shown in Scheme 3, which involves an η^2-C_6D_6 intermediate.[53–57]

The coordination of a C_6D_6 molecule to the unsaturated (44e) pentahydrido complex **6** yielded an intermediary μ-η^2-C_6D_6 complex **I-1** (46e) and a subsequent oxidative addition of the coordinated benzene-d_6 to the adjacent ruthenium center form a phenyl-d_5 derivative **I-2**. Reductive coupling between the phenyl-d_5 group and the hydrido ligand, followed by the liberation of C_6D_5H, would generate **6**-d_1 by way of a μ-η^2-C_6D_5H complex **I-3**. Upon repetition of such an equilibrating process, the hydrido ligands in **6** are exchanged for deuterium to yield **6**-d_6. As far as mononuclear late transition metals, such as rhodium, iridium, and rhenium complexes, are concerned, the intermediacy of the η^2-arene complex in arene C–H activation has been well established.[34] If the H/D exchange reaction between **6** and aromatic compounds proceeds via an η^2-arene intermediate, toluene is expected to be an appropriate probe compound. The H/D exchange at the *para*- and *meta*-positions would precede that at the *ortho*-position, because the steric repulsion between the C_5Me_5 groups surrounding the reaction site and the methyl group attached to



Scheme 3.

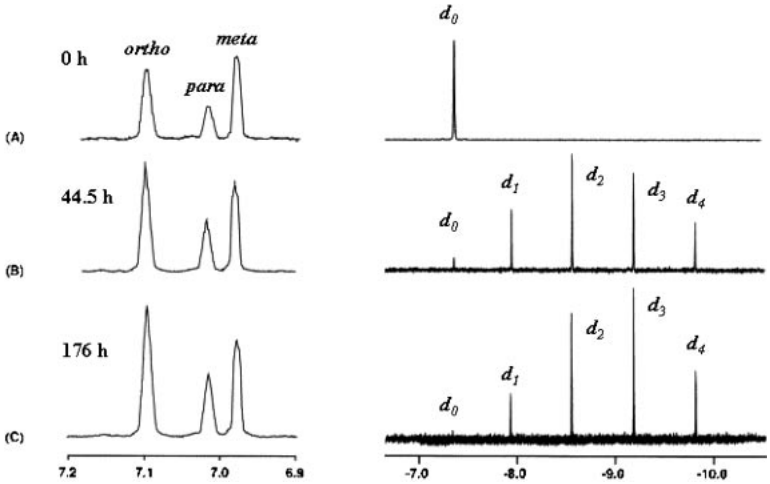


Fig. 4. ^{1}H NMR spectra of the aromatic and the hydride regions in the H/D exchange reaction of **6** with toluene-d_8 at 80 °C.

the aromatic ring largely affected the regiochemistry of the η^2-coordination of the toluene molecule. Thus, we examined the H/D exchange reaction between **6** and toluene-d_8 (Fig. 4). After being heated at 80 °C in toluene-d_8 for 44.5 h, 59% of the hydrides in **6** were exchanged with deuterium atoms, and the isotopomer ratio **6**-d_0/**6**-d_1/**6**-d_2/**6**-d_3/**6**-d_4/**6**-d_5 reached 2/10/25/31/21/11.

Interestingly, only deuterium atoms attached to the aromatic ring carbons of toluene participated in the exchange reaction, and deuterium atoms at the benzylic carbon were not exchanged at all within the experimental errors. The bond-dissociation energy of a benzylic C–H bond (ca. 88 kcal/mol) is much smaller than that of an aromatic C–H bond (ca. 110 kcal/mol);[35] the situation is, of course, almost the same for the corresponding C–D bonds. This result, therefore, strongly suggests that bond cleavage does not proceed via a homolytic process, but via an intermediate arene complex, and that the coordination of toluene via an aromatic C=C bond likely takes place prior to C–D bond cleavage. In the H/D exchange reaction in toluene-d_8, the exchange rate of the deuterium was on the order of *ortho*- (δ 7.10) < *meta*- (δ 6.98) < *para*-position (δ 7.02) and the ratio $k_o/k_m/k_p$ was about 1/2/4. Such regioselectivity was also observed in the H/D exchange reaction between **6** and *o*-xylene-d_{10}. A solution of **6** in *o*-xylene-d_{10} was heated at 80 °C, and the strength of the signals at δ 6.93 and 6.97 was monitored by ^{1}H NMR spectroscopy (Fig. 5).

These two signals are attributable to the aromatic protons contained in the deuterated xylene, and had equal intensity in the initial stage. These two peaks at δ 6.93 (2H) and 6.97 (2H) were unambiguously assigned to ring protons at C-4 and C-5, and those at C-3 and C-6, respectively, based on the INADEQUATE-2D ^{13}C and ^{1}H–^{13}C HSC spectra. With the elapse of time, the formation of the isotopomers **6**-d_n and an increase in the intensity of the two signals at δ 6.93 and 6.97 were observed as a result of the H/D exchange reaction. The methyl protons of *o*-xylene did not participate in the H/D exchange reaction, just as the methyl protons of toluene did not. The intensity of the signal at δ 6.97 increased more rapidly than that of the signal at δ 6.93. The ratio of the exchange rate, $k_{C\text{-}4}/k_{C\text{-}3}$, derived from the increments of the signal intensity at δ 6.97 and 6.93 was about 4.6/1. Based on these observations, we propose that the H/D exchange reaction between **6** and the arenes proceeds by way of an intermediacy of the η^2-arene cluster complex.

The triruthenium pentahydride **6** also underwent H/D exchange with D_2, as did the cationic triruthenium hexahydride **2** and the dinuclear ruthenium tetrahydrido complex **1**. Hydrides coordinated in **6** were completely exchanged for deuterides to generate the corresponding pentadeuterido complex **6**-d_5 when a stirred solution of **6** in tetrahydrofuran was exposed

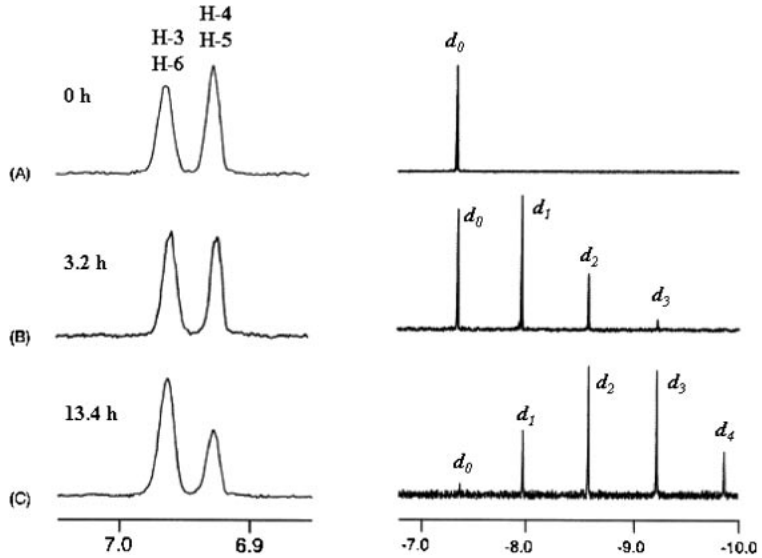
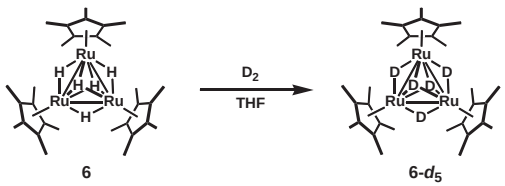


Fig. 5. ^{1}H NMR spectra of the aromatic and the hydride regions in the H/D exchange reaction of **6** with *o*-xylene-d_{10}.

to D_2 at room temperature for 3 h (Eq. 9).



6 **6-d_5** (9)

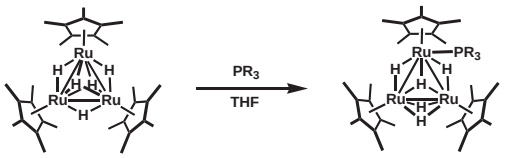
The coordination of C_6D_6 or D_2 to the vacant site, generated as the result of a bonding interaction between the two hydrido ligands, would lead to the oxidative addition of an aromatic C–D or a D–D bond, respectively. While the D_2 molecule is small enough to enter freely into the reaction field of **6**, the molecular size of C_6D_6 is much larger than that of D_2. We, therefore, propose that the rate-determining step of the intermolecular H/D exchange is most probably the step of capture of D_2 or C_6D_6 in the triangular space surrounded by the three C_5Me_5 groups.

Tririutheniumpentahydrido Complex 6 as a Precursor of an Active Species for the "Trimetallic Activation". Reaction of 6 with Small Molecules: A newly synthesized tririutheniumpentahydrido complex **6** is an appropriate candidate for the precursor of an active species for *trimetallic activation*. Here, we use the term "*trimetallic activation*" to refer to one of the activation modes of the substrate in which the synergy of the three metal centers is achieved in the activation step. It is one of the key features of **6** that no carbonyl ligand is included in **6**, irrespective of the bridging or terminal positions. As mentioned previously, the electron density at the metal centers of **6** is, therefore, likely to be higher than that of the polycarbonyl metal clusters or polycarbonylhydrido metal clusters due to coordination of the electron-releasing C_5Me_5 groups. Thus, complex **6** is expected to be much more active than the metal clusters having carbonyl ligands with respect to both coordinative and oxidative addition.

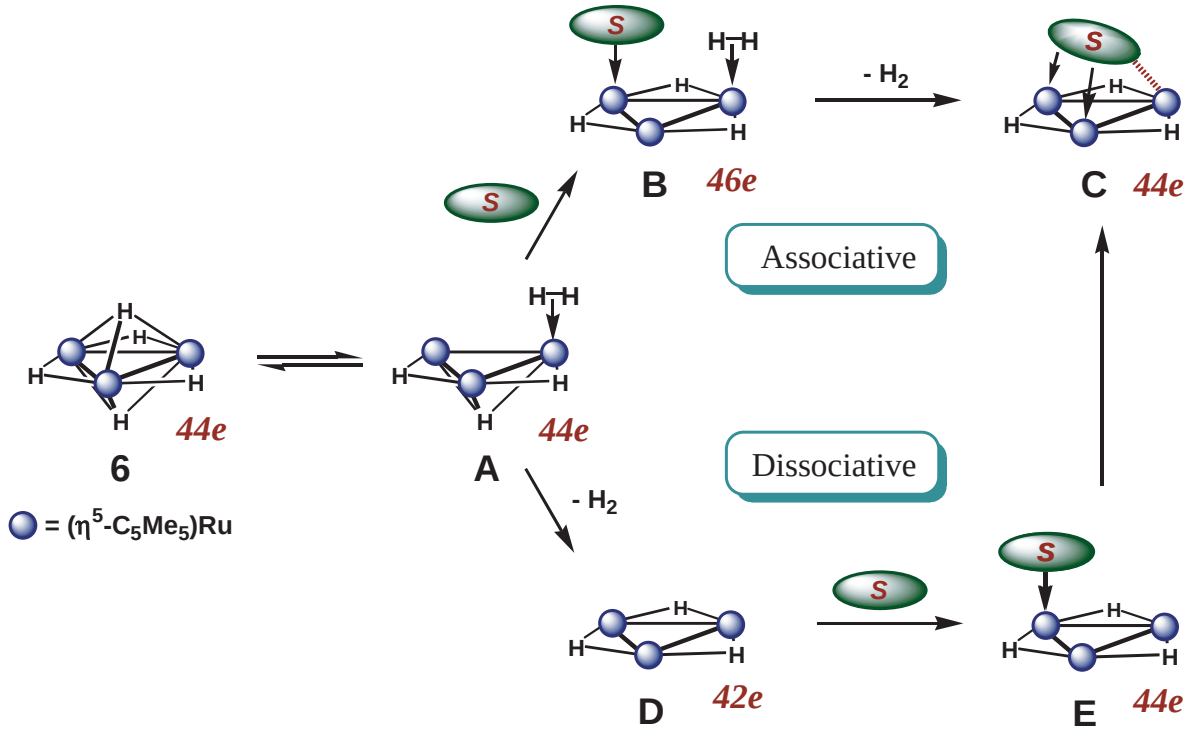
Upon liberation of the hydrides, or making a bonding interaction between the two hydrido ligands to form an η^2-H_2 intermediate, vacant coordination sites would be generated on the Ru_3 plane. Two possible modes of the interaction between the Ru_3 cluster and the substrate are illustrated in Scheme 4. One is an associative path by way of a 46e species (**B**), and the other is a dissociative one that involves a highly unsaturated 42e species (**D**). Regarding the mechanism of the site-exchange process of the hydrido ligands of **6**, we assumed an intermediate species in which the triply bridging hydride has a bonding interaction with the doubly bridging hydride. Such a bonding interaction between the μ_3-hydride and the μ-hydride forms an unsaturated species **A**. The coordination of a substrate to the newly generated vacant coordination site leads to a 46e species **B**, which undergoes the liberation of hydrogen and subsequent bond activation of the substrate to yield **C**. On the other hand, the liberation of hydrogen from **A** prior to coordination of the substrate generates a highly unsaturated 42e species **D**, which activates the substrate by way of a 44e species **E**. The 42e species **D** is probably much more unstable than the 46e species **B** because of its highly unsaturated character. We, therefore, presumed that the activation of the substrate on the reaction site of **6** was achieved by way of the associative path from a stability standpoint.

Although we have, thus far, investigated the reaction chemistry of the trinuclear ruthenium pentahydrido complex **6** through the reaction with hydrocarbons, such as olefins and dienes,[23,58] we have not obtained conclusive evidence concerning the associative pathway of the reaction. However, we fortunately obtained explicit evidence of an associative pathway in the reaction of **6** with phosphines and phosphites.

The reaction of **6** with trimethylphosphine proceeded in tetrahydrofuran at room temperature to result in the formation of a purple solid, which was unambiguously identified as a 1:1-adduct $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_5(PMe_3)]$ (**8a**) based on NMR spectroscopy as well as the analytical data (Eq. 10).



6 **8a (R = Me)** **8b (R = OPh)** (10)



Scheme 4.

The ^{1}H NMR spectrum measured at room temperature revealed four resonance signals at δ −11.82 (d, J = 10.9 Hz), 1.06 (d, J = 8.3 Hz), 1.87 (d, J = 1.8 Hz), and 2.02 (s) ppm in an intensity ratio of 5/9/15/30. These signals were assigned to those of hydrides, coordinated trimethylphosphine, the C_5Me_5 group on the ruthenium atom bound to the phosphine ligand, and two C_5Me_5 groups on the rest of the ruthenium centers, respectively. The five hydrides were observed to be equivalent as a doublet peak with an intensity of 5H at room temperature as the result of a rapid dynamic process, namely, exchange among the μ-coordination sites. The signal of the hydrides broadened with a decrease of the temperature, and split into three broad signals with an intensity ratio of 1/3/1 around δ −3, −11, and −23.5, respectively, at −50 °C. The signal observed around δ −11 with the intensity of 3H further split into two signals as the temperature dropped. At −108 °C, the signals of the hydrides appeared at δ −2.96 (s, 1H), −10.90 (d, J_{PH} = 32.5 Hz, 2H), −11.06 (s, 1H), and −23.50 (s, 1H). The doublet signal at δ −10.90 is assigned to the hydrides bound to the ruthenium atom, which has a direct bonding interaction with the phosphine ligand. The coupling constant of 32.5 Hz is close to the $^{2}J_{PH}$ value observed in the mononuclear hydridophosphineruthenium complex, $Ru(C_5Me_5)(PMe_3)_2H$ ($^{2}J_{PH}$ = 38 Hz).[59] The rest of the hydrido ligands probably bridge the two ruthenium centers that have no bonding interaction with the phosphine ligand. These results clearly show that the reaction of **6** with trimethylphosphine proceeded via an associative pathway to generate the 1:1-adduct **8a**.

Complex **6** also reacted with triphenyl phosphite in a similar manner to result in the formation of **8b**. The ^{1}H NMR spectrum of **8b** showed a marked resemblance to that of **8a**. The signals of the C_5Me_5 groups and the hydrido ligands appeared at δ 2.06, 1.83 (d, J_{PH} = 2.3 Hz), and −11.13 (d, J_{PH} = 10.3 Hz), respectively, with an intensity ratio of 30/15/5. The resonance signals for the coordinated triphenyl phosphite were observed at δ 6.84 (t, 3H), 7.08 (t, 6H), and 7.24 (d, 6H) in the ^{1}H NMR spectrum and δ 134.3 in the ^{31}P NMR spectrum. These results strongly indicate a structural analogy of **8b** with **8a**.

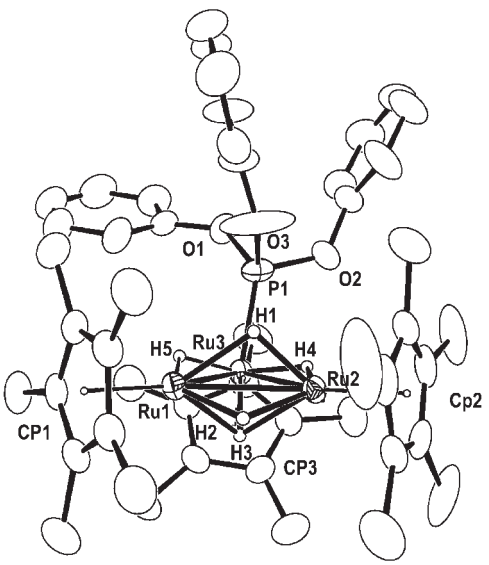


Fig. 6. Thermal ellipsoid representation of [{$Ru(C_5Me_5)$}$_3$-(μ-H)$_5${$P(OPh)_3$}] (**8b**) showing 30% probability ellipsoids. CP is centroid of the C_5Me_5 ring.

The structure of **8b** was unequivocally established by an X-ray diffraction study (Fig. 6). Some of the relevant bond lengths and angles are listed in Table 3.

Figure 6 clearly demonstrates a structure that consists of a triangular Ru_3 core bearing five bridging hydrogen atoms

Table 3. Selected Bond Distances (Å) and Angles (deg) in $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_5\{P(OPh)_3\}]$ (**8b**)

Bond distances			
Ru1–Ru2	2.6504(7)	Ru1–CP1	1.822
Ru1–Ru3	3.0262(6)	Ru2–CP2	1.809
Ru2–Ru3	2.9969(6)	Ru3–CP3	1.893
Ru3–P1	2.1714(14)	P1–O1	1.636(4)
Ru1–H1	1.80(5)	P1–O2	1.630(5)
Ru2–H1	1.84(5)	P1–O3	1.570(5)
Ru3–H1	2.21(5)		
Ru1–H2	1.64(6)	Ru1–H3	1.80(6)
Ru2–H2	1.74(6)	Ru2–H3	1.58(6)
Ru2–H4	1.76(6)	Ru1–H5	1.89(6)
Ru3–H4	1.64(6)	Ru3–H5	1.59(6)
Angles			
Ru1–Ru2–Ru3	64.46(2)	Ru2–Ru3–Ru1	52.21(1)
Ru3–Ru1–Ru2	63.33(2)	P1–Ru3–Ru1	100.01(4)
P1–Ru3–Ru2	92.78(4)		

and a triphenyl phosphite molecule at one of the three ruthenium atoms. The structure of **8b** is approximately in the C_s symmetry with a mirror plane passing through Ru3 and the midpoint of Ru1 and Ru2. Hydrogen atom H4 bridges Ru2 and Ru3 and H5 bridges Ru1 and Ru3, respectively. Two hydrogen atoms, H2 and H3, doubly bind two ruthenium atoms, Ru1 and Ru2. Hydrogen atom H1 is considered to have bonding interaction between the three ruthenium atoms, although one of the three Ru–H distances, Ru3–H1 (2.21(6) Å), is somewhat longer than the others (av. 1.82 Å). The locations of the metal-bound hydrogen atoms are fully consistent with the ^{1}H NMR data of the structurally analogous phosphine complex **8a** recorded at −108 °C. A Ru3–P1 distance of 2.1714(14) Å is in the range of those for the terminally coordinated phosphine and phosphite complexes.

Thus, we proved that the reaction of **6** with tertiary phosphine or phosphite proceeded by way of an associative pathway. The associative pathway is also supported by a theoretical study. Recently, Morokuma proposed an associative pathway in the reaction of **6** with cyclopentadiene[60] based on an ab initio MO calculation.[61]

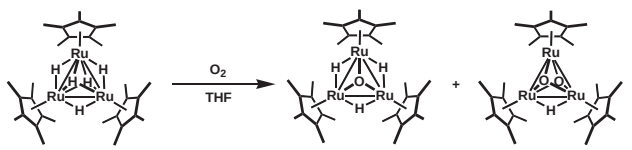
In the case of the Ru_3 framework of **6** being stable enough to be retained during the reaction, the multiple vacant sites generated as a result of H_2 liberation would cooperate in the activation of a substrate.

We confirmed the thermal stability of **6**, as described below. The Ru_3 framework never broke up into a mononuclear or dinuclear species at any significant rate in refluxing tetrahydrofuran, even in the absence of substrates, such as alkenes and alkynes. Furthermore, the reaction of **6** with linear alkanes, such as hexane and octane, proceeded at 170 °C with a retention of the Ru_3 framework to yield a trinuclear *closo*-ruthenacyclopentadiene.[62]

The reactivity of **6** toward alkane strongly depended on the bulkiness of the alkane, and bulky 1,3,5-trimethylcyclohexane put up strong resistance to the C–H bond activation. As a result, compound **6** was quantitatively recovered even when it was heated at 180 °C for 450 h in 1,3,5-trimethylcyclohexane in an autoclave. These results showed that **6** was stable enough to undergo neither fragmentation of the Ru_3 core nor the liberation of hydrido ligands upon heating in solution.

We then examined the reaction of **6** with reactive small molecules, such as dioxygen, CH_3I, and carbon monoxide.

The reaction of **6** with 1.1 equiv of O_2 in a mixed solvent of tetrahydrofuran and methanol (23/1) smoothly proceeded under a temperature range from −78 to −60 °C to form an 88/12 mixture of a trinuclear mono-μ_3-oxo ruthenium complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}O)]$ (**9**), and a di-μ_3-oxo complex, $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)(\mu_3\text{-}O)_2]$ (**10**), while the reaction at higher temperature (−30 °C) formed a 1/1 mixture of these complexes. The addition of methanol to the reaction system was essential for preparing μ_3-oxo complexes **9** and **10** in high yields. Otherwise, the reaction became non-selective and was accompanied by the formation of an unidentified insoluble black solid. As mentioned above, no reaction other than an exchange between the hydrido ligands of **6** and the protonic hydrogen of methanol took place when **6** was treated with methanol. This evidently shows that the μ_3-oxo ligands in **9** and **10** do not stem from methanol, but from dioxygen. Although we failed to synthesize the mono-μ_3-oxo complex **9** selectively in the reaction of **6** with dioxygen, we successfully separated analytically pure **9** as dark-green crystals in 39% yield from 88/12 mixtures of **9** and **10** by crystallization from a cooled (−30 °C) tetrahydrofuran solution. The mono-μ_3-oxo complex **9**, as well as **6**, is very sensitive to dioxygen. Monitoring the reaction of the isolated mono-μ_3-oxo complex **9** with an equimolar amount of dioxygen by ^{1}H NMR spectroscopy confirmed the immediate and quantitative formation of the di-μ_3-oxo complex **10**. Compound **10** was, of course, the exclusive product in the reaction of **6** with a large excess of dioxygen. The results of the reaction of **6** with dioxygen are summarized by the following equation (Eq. 11).



(11)

An ethyltetramethylcyclopentadienyl analogue of the di-μ_3-oxo complex, $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)(\mu_3\text{-}O)_2]$ (**10′**), was similarly obtained in quantitative yield upon the treatment of **6′** with 2 equiv of dioxygen in tetrahydrofuran. In the reaction of **6** with molecular oxygen, a single oxygen atom stemmed from dioxygen was incorporated into the complex as a μ_3-oxo ligand, and the second oxygen atom was reduced by the hydrido ligands to form water. The formation of water in the reaction could not be confirmed when the reaction of **6** with 2 moles of dioxygen in tetrahydrofuran-d_8 was monitored by means of ^{1}H NMR spectroscopy. However, the IR spectra and the analytical data of the freshly obtained di-μ_3-oxo complexes **10** and **10′** showed the inclusion of a water molecule in them as the solvent of crystallization. As mentioned below, a single-crystal X-ray diffraction study of **10′** clearly showed the presence of a water molecule held by hydrogen bonds.

The ^{1}H NMR spectrum of **9** revealed two singlet signals attributable to the C_5Me_5 ligand and the hydrides at δ 1.80 and

−11.51, respectively, in an intensity ratio of 45H/3H. Thus, the three C_5Me_5 groups in **9** were observed to be equivalent in both the ^1H and ^{13}C NMR spectra, whereas there were two inequivalent resonances for the C_5Me_5 ligands in **10**, which appeared at δ 1.78 (15H) and 1.76 (30H). This implies that compound **9** has a symmetry element that relates the three ruthenium atoms; most likely, this is a three-fold rotation axis that passes through the triply-bridging oxygen atom, and is perpendicular to the plane of the three ruthenium atoms. In contrast, a symmetry element included in the di-μ_3-oxo complex **10** is a mirror plane that bisects one of the Ru–Ru bonds and passes through the two bridging oxygen atoms. The molecular structures of **9**, **10**, and **10′** were confirmed by means of single-crystal X-ray diffraction studies.

Crystals of **9** were obtained from cooled (−30 °C) tetrahydrofuran. However, we encountered a bothersome problem; namely, compounds **9** and **6** crystallized as mixed crystals when μ_3-oxo complex **9** contained a small amount of unreacted **6** as an impurity. Because single crystals of **9** and **6** both conform to the triclinic space group $P\bar{1}$, and their cell parameters are very similar to each other, they often crystallizes as mixed crystals. The purity of the crystals used for the X-ray structure determination should, therefore, be checked by means of ^1H NMR spectroscopy prior to a diffraction study. After repeated efforts, we were fortunately able to obtain single crystals of **9**. Data collection and refinement proceeded without any problem, and the refinement converged with a residual of $R_1 = 0.0315$ ($wR_2 = 0.0702$).

Reasonably-sized single crystals of di-μ_3-oxo complex **10** were obtained from tetrahydrofuran at −30 °C. In this case, the data collection, itself, proceeded without any problem, but refinement was unsuccessful because of the presence of disordered water molecules that were bound to μ_3-oxo ligands with hydrogen bonding. Several attempts to refine the structure were in vain, but single crystals of **10** free of water molecules were fortunately recovered from the reaction mixture of **10** with ethylene in tetrahydrofuran. The crystals were suitable for X-ray structural determination, and data collection and refinement went well. In all cases, hydrogen atoms bonded to the ruthenium atoms were not located in the differential Fourier maps.

The structures of **9**, **10**, and **10′** are displayed in Figs. 7–9. Tables 4–6 list some of the relevant bond distances and angles.

The triply bridging oxygen atom in the mono-μ_3-oxo complex **9** is disordered between the two positions, O1 and O2 (55.0/45.0). In the case of the di-μ_3-oxo complex **10′**, water molecules are included in the unit cell, and the oxygen atom is disordered between O3 and O4. The occupancies of O3 and O4 are both 0.5, and they are bound to O1 and O2, respectively, by hydrogen bonding. The O1–O3 and O2–O4 distances of 2.822(6) and 2.738(6) Å, respectively, are comparable to the reported value for the hydrogen bonded O–H···O system.[63]

The average Ru–Ru distances in the di-μ_3-oxo complexes **10** (2.7135(10) Å) and **10′** (2.7164(4) Å) are slightly longer than that observed in the mono-μ_3-oxo complex **9** (2.7028(8) Å). This can possibly be explained according to the EAN rule applied to **10** (48e), **10′** (48e), and **9** (46e). The average Ru–O distances of 1.958(6) and 1.953(7) Å for

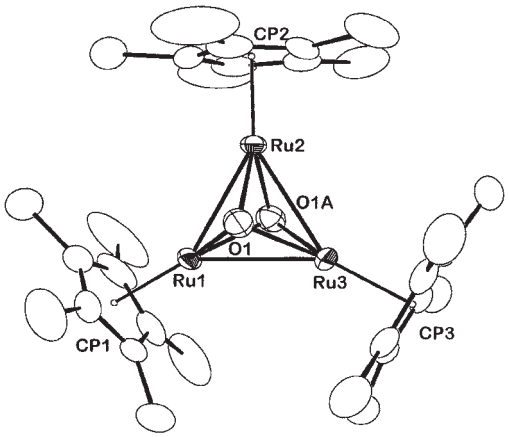


Fig. 7. Thermal ellipsoid representation of [{Ru(C_5Me_5)}$_3$-(μ-H)$_3$(μ_3-O)] (**9**) showing 30% probability ellipsoids. CP is centroid of the C_5Me_5 ring.

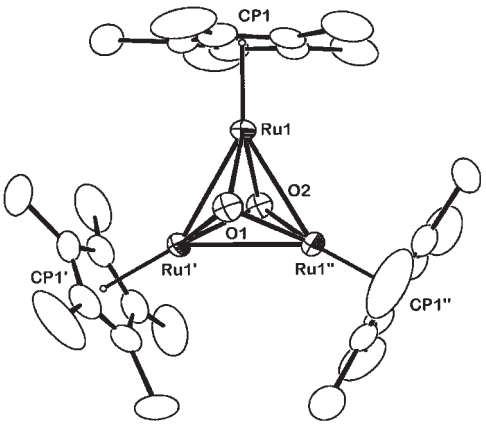


Fig. 8. Thermal ellipsoid representation of [{Ru(C_5Me_5)}$_3$-(μ-H)(μ_3-O)$_2$] (**10**) showing 30% probability ellipsoids. CP is centroid of the C_5Me_5 ring.

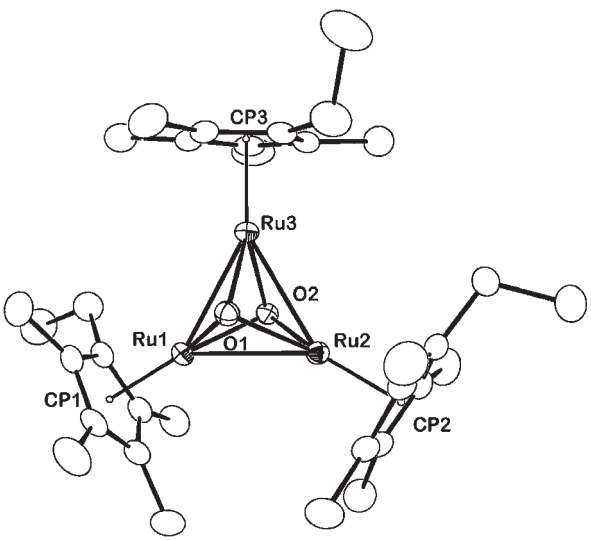


Fig. 9. Thermal ellipsoid representation of [{Ru(C_5Me_4Et)}$_3$(μ-H)(μ_3-O)$_2$] (**10′**) showing 30% probability ellipsoids. Oxygen atom of hydrogen-bonded water is disordered between two positions, O3 and O4 (50/50). CP is centroid of the C_5Me_5 ring.

Table 4. Selected Bond Distances (Å) and Angles (deg) in $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}O)]$ (**9**)

Bond distances			
Ru1–Ru2	2.6989(9)	Ru1–CP1	1.827
Ru1–Ru3	2.7005(6)	Ru2–CP2	1.826
Ru2–Ru3	2.7089(8)	Ru3–CP3	1.833
Ru1–O1	1.963(6)	Ru1–O1A	1.949(7)
Ru2–O1	1.961(6)	Ru2–O1A	1.945(8)
Ru3–O1	1.964(6)	Ru3–O1A	1.950(7)
Angles			
Ru1–Ru2–Ru3	59.92(2)	Ru1–O1–Ru2	86.9(2)
Ru2–Ru3–Ru1	59.86(2)	Ru2–O1–Ru3	87.3(2)
Ru3–Ru1–Ru2	60.23(2)	Ru3–O1–Ru1	86.9(2)
Ru1–O1A–Ru2	87.8(3)		
Ru2–O1A–Ru3	88.1(3)		
Ru3–O1A–Ru1	86.9(2)		

Table 5. Selected Bond Distances (Å) and Angles (deg) in $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)(\mu_3\text{-}O)_2]$ (**10**)

Bond distances			
Ru1–Ru1′	2.7135(10)	Ru1–CP1	1.828
Ru1–O1	2.013(6)	Ru1–O2	1.995(5)
O1–O2	2.499		
Angles			
Ru1′–Ru1–Ru1″	60.0	Ru1–O1–Ru1′	84.8(3)
O1–Ru1–O2	77.2(3)	Ru1–O2–Ru1″	85.7(3)

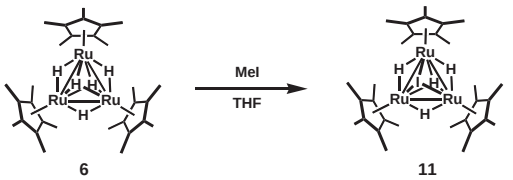
Table 6. Selected Bond Distances (Å) and Angles (deg) in $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)(\mu_3\text{-}O)_2]$ (**10′**)

Bond distances			
Ru1–Ru2	2.7211(4)	Ru1–CP1	1.813
Ru1–Ru3	2.7169(4)	Ru2–CP2	1.812
Ru2–Ru3	2.7103(4)	Ru3–CP3	1.811
Ru1–O1	2.0203(17)	Ru1–O2	2.0172(16)
Ru2–O1	2.0158(17)	Ru2–O2	2.0156(16)
Ru3–O1	2.0210(17)	Ru3–O2	2.0239(16)
O1–O2	2.543	O1–O3	2.84
O2–O4	2.75		
Angles			
Ru1–Ru2–Ru3	60.029(11)	Ru1–O1–Ru2	84.78(6)
Ru2–Ru3–Ru1	60.183(11)	Ru2–O1–Ru3	84.35(6)
Ru3–Ru1–Ru2	59.788(11)	Ru3–O1–Ru1	84.49(6)
Ru1–O2–Ru2	84.87(6)		
Ru2–O2–Ru3	84.28(6)		
Ru3–O2–Ru1	84.49(6)		

Ru–O1 and Ru–O1A in **9**, respectively, are significantly shorter than those observed in the di-μ_3-oxo complexes **10** (2.004(6) Å) and **10′** (2.019(2) Å). These values, however, still lie within the range of those for the metal–oxygen bond in μ_3-oxo and di-μ_3-oxo complexes of transition metals.[64–69]

There are several precedents of trinuclear mono- and di-μ_3-oxo complexes of late transition metals derived from a polycarbonyl cluster by a reaction with dioxygen.[66,69–71] The preparation method of the μ_3-oxo complexes **9**, **10**, and **10′** is essentially similar to that for the polycarbonyl clusters, but is the first example of the oxygenation method applied to polyhydridometal clusters.

The reaction of **6** with iodomethane in tetrahydrofuran smoothly proceeded at room temperature to result in the generation of a novel trinuclear tetrahydrido complex, $[\{Ru(C_5Me_5)\}_3(\mu_3\text{-}H)(\mu\text{-}H)_3(\mu_3\text{-}I)]$ (**11**), in which an iodido ligand triply bridged ruthenium atoms (Eq. 12).



6 11 (12)

Compound **11** was unambiguously identified on the basis of ^{1}H and ^{13}C NMR spectral data as well as elemental analysis. Resonance signals for the C_5Me_5 groups and the hydrido ligands appeared as singlet peaks at δ 2.12 (45H) and −2.25 (4H), respectively, in the ^{1}H NMR spectrum recorded at 25 °C. Resonance for the three C_5Me_5 groups was observed to be equivalent as a sharp singlet peak in the temperature range from 25 to −110 °C, while the singlet signal for the hydride ligands was significantly broadened at low temperature. This result implies that **11** has a threefold rotation axis in the molecule. The signal for the three C_5Me_5 groups are, therefore, observed to be equivalent irrespective of the fluxional behavior of the hydrides. Temperature-dependent resonance signals for the four hydrido ligands are most likely to be due to a rapid exchange of the hydrides among the coordination sites, that is, among the μ_3-site and the three μ_2-sites. The rapid site-exchange of the hydrido ligands was confirmed by ^{1}H NMR spectroscopy. With a decrease of temperature, the line width at the half-height of the signal for the hydrido ligands significantly broadened. The line-widths were 9.0, 36.1, 180.1, and 802.8 Hz at 27, −20, −55, and −80 °C, respectively. The signal for hydrides was flattened near −110 °C. We could not, however, observe decoalescence of the hydrido resonance into two signals with an integral intensity ratio of 3/1.

When the reaction of **6** with 0.9 equiv of iodomethane in tetrahydrofuran-d_8 was monitored by means of ^{1}H NMR spectroscopy, no reaction intermediates were detected, and a sharp singlet signal of the formed methane was observed at δ 0.19 together with the signals of **11**. The formation of methane seems most likely to be due to the oxidative addition of iodomethane to one of the ruthenium centers and subsequent reductive coupling between the methyl ligand and the hydride. The reductive elimination of methane from the triruthenium cluster must be an energetically favored process compared to that of dihydrogen or hydrogen iodide, as established in the chemistry of the mononuclear complex.

In order to determine the structure of **11**, an X-ray crystallographic study was carried out on a black-brown, needle-like crystal obtained by cooling a tetrahydrofuran–pentane solution of **11** to −20 °C. The structure of **11** is shown as ORTEP diagrams in Fig. 10. Selected bond distances and bond angles are given in Table 7.

Notable features of the structure include a pseudo tetrahe-

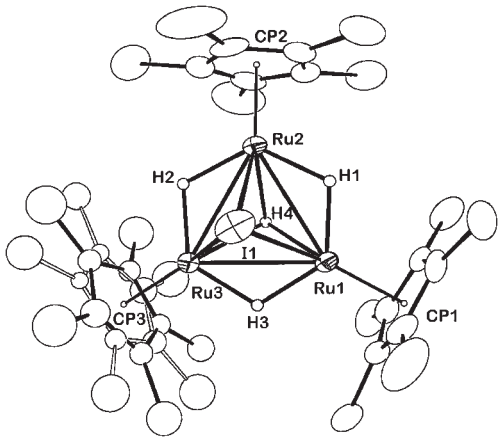


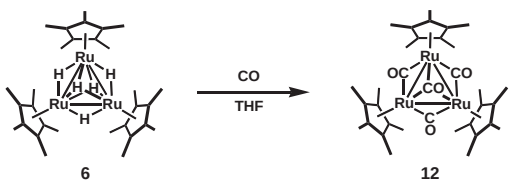
Fig. 10. Thermal ellipsoid representation of [{Ru(C_5Me_5)}$_3$(μ-H)$_3$(μ_3-H)(μ_3-I)] (**11**) showing 30% probability ellipsoids. CP is centroid of the C_5Me_5 ring.

Table 7. Selected Bond Distances (Å) and Angles (deg) in [{Ru(C_5Me_5)}$_3$(μ_3-H)(μ-H)$_3$(μ_3-I)] (**11**)

Bond distances			
Ru1–Ru2	2.8665(12)	Ru1–CP1	1.803
Ru1–Ru3	2.8642(12)	Ru2–CP2	1.802
Ru2–Ru3	2.8651(13)	Ru3–CP3	1.789
Ru1–I1	2.8500(13)	Ru–μ-H	1.70 (av)
Ru2–I1	2.8461(13)	Ru–μ_3-H	2.08 (av)
Ru3–I1	2.8486(14)		
Angles			
Ru1–Ru2–Ru3	59.96(3)	Ru1–I1–Ru2	60.43(3)
Ru2–Ru3–Ru1	60.04(2)	Ru2–I1–Ru3	60.41(3)
Ru3–Ru1–Ru2	59.99(3)	Ru3–I1–Ru1	60.35(3)

dral Ru_3I core with average Ru–Ru and Ru–I distances of 2.8653(12) and 2.8482(13) Å, respectively. Complex **11** is a 48e cluster, as are complexes **10** and **10′**, and the EAN rule applied to these complexes requires a metal–metal single bond between the ruthenium atoms. Thus, the interatomic distances between the ruthenium atoms in **11** correspond to a Ru–Ru single bond. The significantly short Ru–Ru bond lengths in **10** and **10′**, compared to those in **11**, are probably due to the presence of two triply bridging 4e ligands, μ_3-oxo groups, which tightly bind the ruthenium atoms.

Pentahydrido complex **6** smoothly reacted with atmospheric pressure of carbon monoxide to generate a paramagnetic tetracarbonyl complex, [{Ru(C_5Me_5)}$_3$(μ-CO)$_3$(μ_3-CO)] (**12**), with a retention of the trinuclear metallic framework (Eq. 13).



6 12 (13)

Although we could not obtain a well-resolved ^{1}H NMR spectrum of **12**, because of its paramagnetic character, it was unambiguously assigned on the basis of IR, FD-MS, as well as elemental analysis. The IR spectrum of **12** reveals strong absorption attributable to the stretching vibrations of the bridging carbonyl ligands at 1782, 1735, and 1615 cm^{-1}. The absorption at 1615 cm^{-1} is due to the triply bridging carbonyl group. This value is comparable to the reported values of 1689, 1627, and 1626 cm^{-1} for [Ru_3(μ_3-O)(μ_3-CO)(CO)$_5$(μ-dppm)$_2$],[66] [Ru_3(μ_3-O)(μ_3-CO)(CO)$_3$(μ-dppm)$_3$],[69] and [Ru_3(μ_3-O)-(μ_3-CO)(CO)$_3$(μ-dppm)]Cl,[69] respectively. In the field-desorption mass spectrum of **12**, the intensities of the obtained isotopic peaks for $C_{34}H_{45}O_4Ru_3$ were in agreement with the calculated values within the experimental error. The proposed molecular structure was confirmed by means of X-ray crystallography. The shapes of the black-green single crystals of **12**, obtained from tetrahydrofuran at -34 °C, were thin plates, and were not suitable for a diffraction study. Although the full-matrix least-squares refinement did not sufficiently converge ($R_1 = 0.148$, $wR_2 = 0.386$), a preliminary result clearly elucidated the atom connectivity of the structure.

Thus, the three ruthenium atoms in **6** appeared to be tightly bound to each other so as not to split up into three mononuclear species in the reaction with reactive small molecules, such as O_2, CH_3I, and CO.

In conclusion, we have synthesized a cationic triruthenium hexahydrido complex, [{Ru(C_5Me_5)}$_3$(μ-H)$_6$](Y) (**2**: Y = BF_4, CF_3SO_3, 1/2(SO_4), $C_6H_5CO_2$, CH_3CO_2), by the treatment of diruthenium tetrahydride [{Ru(C_5Me_5)}$_2$(μ-H)$_4$] (**1**) with the corresponding acid. The protonation of **1** and a subsequent liberation of dihydrogen from the resulting dicationic hexahydrido species led to the intermediary dicationic tetrahydrido complex, [{Ru(C_5Me_5)}$_2$(μ-H)$_4$]$^{2+}$(Y)$_2$ (**B**), which is in equilibrium with a mononuclear monocationic dihydrido complex, [Ru(C_5Me_5)(μ-H)$_2$]$^+$(Y) (**C**), in diethyl ether, and reacted instantly with **1** to yield the trinuclear complex **2**. This mechanism involving the highly unsaturated cationic species **C** was proved by the reaction of **1** with acid HY in the presence of benzene or acetonitrile, which yielded the corresponding mononuclear cationic complex, [Ru(C_5Me_5)(C_6H_6)](Y) or [Ru(C_5Me_5)(CH_3CN)$_3$](Y), respectively.

The treatment of the trinuclear cationic complex **2** with a base, such as CH_3ONa, generated the triruthenium pentahydrido complex **6**, which has two μ_3-H and three μ-H ligands. The hydrides in **6** rapidly exchange the coordination sites with each other in solution, even at low temperature, probably by way of an intermediary η^2-H_2 species generated as the result of a bonding interaction between the two hydrido ligands. The tendency to generate the intermediary η^2-H_2 species is probably responsible for the high reactivity of **6**.

Pentahydrido complex **6** readily undergoes an intermolecular H/D exchange reaction with D_2 or C_6D_6. As the result of a detailed analysis using ^{1}H NMR spectroscopy, it was proposed that the H/D exchange reaction with deuterated arenes, such as C_6D_6, $C_6D_5CD_3$, and $C_6D_4(CD_3)_2$, is likely to proceed via an η^2-arene intermediate.

Pentahydrido complex **6** is a coordinatively unsaturated 44e complex and, which is a suitable and useful precursor of the active species for *trimetallic activation*. To elucidate the initial step of the reaction of **6**, the reaction with trimethylphosphine was examined. The exclusive formation of [{Ru(C_5Me_5)}$_3$(μ-H)$_5$(PMe_3)] (**8a**) in a reaction performed at room temperature

showed that the reaction proceeded via an associative path. The above-mentioned H/D exchange reaction between C_6D_6 and the hydrides in **6** is also associative, and presumably begins with a coordinative addition of C_6D_6 to one of the ruthenium centers in an η^2-fashion.

Thus, the generation of a vacant site at the ruthenium center and an intramolecular site-exchange of the hydride are closely correlated by the formation of the intermediate η^2-H_2 species. The activation parameters for the site-exchange of the hydrido ligands is, therefore, one of the measures of the reactivity in the intermolecular process of the polyhydrido cluster. Actually, we have recently proposed a tentative correlation between the activation parameters for the site-exchange of the hydrido ligands and that for the H/D exchange between the hydrides and D_2 in the heterobimetallic complex, $[Re(C_5Me_5)(H)_2(\mu\text{-}H)_3Ru(C_5Me_5)]$, and $[Re\{CH_3C(CH_2PPh_2)_3\}(H)(\mu\text{-}H)_3Ru(C_5Me_5)]$.[72]

The thermal stability of the Ru_3 framework of **6** was also demonstrated by heating **6** in 1,3,5-trimethylcyclohexane at 180 °C. Complex **6** underwent neither fragmentation of the Ru_3 core nor liberation of the hydrido ligand. The trinuclear framework of **6** is sufficiently stable to react with reactive small molecules, such as dioxygen, iodomethane, and carbon monoxide with retention of the framework of the cluster.

Thus, complex **6** has electron-donating C_5Me_5 groups, and the multiple hydrido ligands suitable for generating the vacant coordination site and its Ru_3 framework is extremely stable in solution, even at high temperature. Complex **6** is, therefore, capable of activating a substrate in a concerted manner, such that the three metal centers in **6** are allotted respective roles as the coordination site and the activation site in the substrate-activation step.

Experimental

General. All of the manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, toluene-d_8, benzene, benzene-d_6, tetrahydrofuran, tetrahydrofuran-d_8, 1,2-dimethoxyethane, diethyl ether, and pentane were dried over Na/benzophenone. Chloroform-*d* and dichloromethane-d_2 were dried over calcium hydride and stored over 4 Å molecular sieves. $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]$ was prepared according to previously published procedures.[23] All other chemicals were of reagent grade, and were purified according to standard procedures, as necessary. The alumina (Merck Art. 1097) used for column chromatography was deoxygenated under a vacuum prior to use. Proton and ^{13}C NMR spectra were recorded on JEOL GX-500, JEOL EX-270, Varian Gemini 300, and Varian Unity Inova 400 Fourier-transform spectrometers with tetramethylsilane as an internal standard. Variable-temperature ^1H NMR spectra were recorded on JEOL GX-500 and Varian Unity Inova 400 spectrometers. The chemical shifts are reported in parts per million (δ), the coupling constants are reported in hertz (Hz) and the integrations are reported in according to the number of protons. The IR spectra were recorded on a JASCO FT/IR-5000 spectrophotometer, and the frequencies were reported in cm^{-1}. Field-desorption mass spectra were recorded on a Hitachi GC-MS M80 high-resolution mass spectrometer. Mass-spectral results were reported in m/z using the most intense peak in each envelope. 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 **2g**, **6**, **9**, and **10** were obtained as described in the text, and that of **10′** was obtained as described below. They were mounted on glass fibers. X-ray diffraction measurements were performed on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo Kα ($\gamma = 0.71069$ Å) radiation. Intensity data were collected using a $\omega/2\theta$ scan technique; 3 standard reflections were recorded every 150 reflections. The data were processed using the TEXSAN crystal solution Package operating on an IRIS Indigo computer.[73] Neutral atom scattering factors were obtained from the standard sources.[74] In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data for each structure.

Structure Solution and Refinement for 2g, 6, 9, 10, and 10′. The positions of the Ru atoms were determined using direct methods employing the PATTY direct-method routines.[75] In each case, the non-hydrogen atoms were located from successive difference Fourier map calculations using the DIRDIF-92 programs,[75] and were refined anisotropically by using full-matrix least-squares techniques on F^2. In the case of **2g**, **6**, and **10′**, the positions of hydrogen atoms bonded to the Ru atoms were located by sequential difference Fourier synthesis, and were refined isotropically. The crystal data and the results of the analyses are listed in Table 8.

Reaction of 1 with Tetrafluoroboric Acid. To a 50-mL Schlenk tube charged with $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]$ (196 mg, 0.412 mmol) and tetrahydrofuran (10 mL), $HBF_4 \cdot Et_2O$ (85 wt % in Et_2O) (84 μL, 0.49 mmol) was added at −78 °C. The mixture was gradually warmed to room temperature and stirred for 1 h. The red suspension turned brown-purple with evolution of dihydrogen as the mixture was warmed. After removal of the solvent under reduced pressure, the brown-purple residual solid was purified by column chromatography on alumina with tetrahydrofuran to give $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](BF_4)$ (**2a**) (207 mg, 94%) as a brown-purple crystalline solid. Although this material appeared to be pure by ^1H NMR, several attempts to obtain satisfactory elemental analyses were unsuccessful. **2a**: ^1H NMR (270 MHz, 23 °C, $CDCl_3$) δ −11.23 (s, 6H, Ru–*H*–Ru), 1.99 (s, 45H, Cp–*Me*). $^{13}C\{^1H\}$ NMR (67.5 MHz, 23 °C, $CDCl_3$) δ 12.1 (Cp–*Me*), 97.7 (Cp-*ring*). T_1 (500 MHz, CD_2Cl_2): 849 ms (at 20 °C), 513 ms (at −20 °C), 274 ms (at −50 °C), and 387 ms (at −80 °C). IR (KBr, cm^{-1}): 2983, 2901, 1489, 1459, 1424, 1378, 1091, 1046, 1018, 630.

Reaction of 1 with Trifluoromethanesulfonic Acid. To a suspension of $[\{Ru(C_5Me_5)_2(\mu\text{-}H)_4\}]$ (339 mg, 0.712 mmol) in tethahydrofuran (10 mL) was added CF_3SO_3H (1.0 M in Et_2O) (1.03 mL, 1.03 mmol) at 25 °C with vigorous stirring. The color of the solution changed from red to deep purple along with the evolution of hydrogen. After being stirred for 2 h at room temperature, the solvent was removed under reduced pressure from the reaction mixture. Washing the brown-purple residual solid with diethyl ether (20 mL × 5) yielded $[\{Ru(C_5Me_5)(\mu\text{-}H)_2\}_3](CF_3SO_3)$ (**2b**) (375 mg, 92%) as a brown-purple crystalline solid. **2b**: ^1H NMR (270 MHz, 23 °C, $CDCl_3$) δ −11.24 (s, 6H, Ru–*H*–Ru), 1.99 (s, 45H, Cp–*Me*). $^{13}C\{^1H\}$ NMR (67.5 MHz, 23 °C, $CDCl_3$) δ 12.1 (Cp–*Me*), 97.7 (Cp-*ring*), 120.5 (q, $J_{CF} = 320.9$ Hz, CF_3SO_3). IR (KBr, cm^{-1}): 2951, 2894, 1457, 1424, 1373, 1254, 1217, 1137, 1085, 1021, 795, 748, 632, 570, 518. Anal. Calcd for $C_{31}H_{51}O_3F_3SRu_3$: C, 43.07; H, 5.95%. Found: C, 42.86; H, 6.14%.

Reaction of 1 with Sulfuric Acid. To a suspension of $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]$ (223 mg, 0.467 mmol) in tetrahydrofuran

Table 8. Crystallographic Data for **2g**, **6**, **8b**, **9**, **10**, **10′**, and **11**

	2g	**6**	**8b**	**9**	**10**	**10′**	**11**
Formula	$C_{42}H_{75}F_6O_6PRu_3$	$C_{30}H_{50}Ru_3$	$C_{55}H_{73}O_3PRu_3$	$C_{30}H_{48}ORu_3$	$C_{30}H_{46}O_2Ru_3$	$C_{33}H_{54}O_3Ru_3$	$C_{30}H_{49}IRu_3$
Formula weight	1124.20	713.91	1116.35	727.89	740.87	802.00	839.80
Cryst size/mm	0.30 × 0.25 × 0.20	0.40 × 0.40 × 0.20	0.30 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.20	0.20 × 0.15 × 0.10
Crystal system	triclinic	triclinic	monoclinic	triclinic	trigonal	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$
a/Å	15.622(3)	11.076(3)	17.973(3)	11.055(3)	18.555(3)	12.6920(17)	11.0807(17)
b/Å	16.274(4)	15.342(3)	16.0387(15)	15.463(4)	18.555(3)	13.5363(17)	18.150(4)
c/Å	10.997(3)	11.070(3)	18.761(4)	11.042(2)	15.756(7)	11.3209(17)	8.4955(19)
α/deg	109.492(18)	108.551(19)	90	108.756(18)	90	108.927(11)	95.324(18)
β/deg	109.872(18)	119.506(15)	119.580(13)	119.580(13)	90	104.644(11)	108.763(14)
γ/deg	91.162(19)	73.258(18)	90	72.92(2)	120	98.585(11)	89.969(16)
V/Å^3	2450.1(10)	1532.3(6)	5162.0(15)	1533.4(6)	4698(2)	1722.3(4)	1610.0(5)
Z	2	2	4	2	6	2	2
D_{calcd}/g cm^{-1}	1.524	1.547	1.436	1.576	1.571	1.547	1.732
Temp/K	297	293	293	292	297	293	297
μ(Mo Kα)/cm^{-1}	10.09	14.74	9.38	14.77	1.451	13.27	23.63
Diffractometer	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-5R
Radiation	Mo Kα ($\lambda = 0.71069$)	Mo Kα ($\lambda = 0.71069$)	Mo Kα ($\lambda = 0.71069$)	Mo Kα ($\lambda = 0.71069$)	Mo Kα ($\lambda = 0.71069$)	Mo Kα ($\lambda = 0.71069$)	Mo Kα ($\lambda = 0.71069$)
Monochromator	graphite	graphite	graphite	graphite	graphite	graphite	graphite
$2\theta_{max}$/deg	50	55	50	55	55	55	55
No. of rflns collected	8923	9143	9365	5675	2913	6348	7564
No. of indep rflns	8582	8717	9049	5371	1818	6054	7333
No. of rflns obsd ($>2\sigma$)	6635	6558	6911	4386	1282	5448	3130
$R1$ ($I > 2\sigma(I)$)	0.0453	0.0356	0.0370	0.0315	0.0502	0.0206	0.0509
$wR2$ ($I > 2\sigma(I)$)	0.1176	0.0707	0.0867	0.0702	0.1190	0.0508	0.1151
$R1$ (all data)	0.0700	0.0635	0.0637	0.0476	0.0874	0.0259	0.2002
$wR2$ (all data)	0.1296	0.0773	0.1025	0.0753	0.1332	0.0530	0.1541
No. of params	498	331	595	318	107	387	276
GOF	1.021	1.024	1.051	1.035	0.979	1.038	0.933
Max and min. peaks in final diff map/e$^-$ Å^{-3})	1.150; −0.519	0.799; −0.689	1.124; −1.002	0.405; −0.466	1.382; −0.537	0.504; −0.437	1.076; −0.777

(10 mL) was added H_2SO_4 (0.20 M in Et_2O) (2.5 mL, 0.50 mmol) at 25 °C with vigorous stirring. After being stirred for 3 h at room temperature, the solvent was removed under reduced pressure from the reaction mixture. Washing the brown-purple residual solid with diethyl ether (20 mL × 5) afforded [{Ru(C_5Me_5)}$_3$(μ-H)$_6$](1/2SO_4 + H_2SO_4) (**2c**) (261 mg, 97%) as a brown-purple crystalline solid. The incorporation of sulfuric acid in **2c** was confirmed by ^{1}H NMR. **2c**: ^{1}H NMR (270 MHz, 23 °C, $CDCl_3$) δ −11.23 (s, 6H, Ru–*H*–Ru), 2.00 (s, 45H, Cp–*Me*), 5.9 (br, 2H, H_2SO_4). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, $CDCl_3$) δ 12.1 (Cp–*Me*), 97.6 (Cp-*ring*). IR (KBr, cm^{-1}): 3500–3000 ($\nu_{OH\cdots O}$), 2974, 2955, 2898, 1463, 1373, 1357, 1253 (ν_{SO}), 1228 (ν_{SO}), 1102, 1062, 1013, 850, 759, 718, 636, 607, 576, 425. The amount of sulfuric acid incorporated in **2c** was changed according to the amount used in the reaction. Therefore, several attempts to obtain satisfactory elemental analyses were unsuccessful.

Reaction of 1 with Benzoic Acid. To a 50-mL Schlenk tube charged with [{Ru(C_5Me_5)}$_2$(μ-H)$_4$] (159 mg, 0.333 mmol) and C_6H_5COOH (82 mg, 0.67 mmol) was added tethahydrofuran (10 mL). After stirring for 3 days at room temperature, the mixture became red-orange and homogeneous. The solvent was removed in vacuo. The resulting brown-red residue was extracted with diethyl ether (10 mL × 5) to leave [{Ru(C_5Me_5)}$_3$(μ-H)$_6$]($C_6H_5CO_2$) (**2d**) (48 mg, 26%) as a brown-purple solid. The resulting solution was filtered through a Celite pad, and dried in vacuo to afford [{Ru(C_5Me_5)}$_2$(μ-H)$_2$(μ-OCOC_6H_5)$_2$] (**3d**) (170 mg, 71%) as a red-orange solid. **2d**: ^{1}H NMR (270 MHz, 23 °C, CD_2Cl_2) δ −11.26 (s, 6H, Ru–*H*–Ru), 1.98 (s, 45H, Cp–*Me*), 7.30–7.54 (m, 3H, *Ph*), 8.11 (d, J = 7.1 Hz, 2H, *Ph*). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, CD_2Cl_2) δ 12.2 (Cp–*Me*), 97.7 (Cp-*ring*), 120.3 (*Ph*), 128.3 (*Ph*), 130.1 (*Ph*), 133.0 (*Ph*), 169.9 (Ph–*C*O–). IR (KBr, cm^{-1}): 2996, 2948, 2891, 2856, 1699 (ν_{CO}), 1592, 1444, 1371, 1359, 1307, 1256, 1167, 1091, 1063, 1015, 854, 805, 781, 712, 649, 641. Although this material appeared to be pure by ^{1}H NMR, several attempts to obtain satisfactory elemental analyses were unsuccessful because of its instability, even in the solid state. **3d**: ^{1}H NMR (270 MHz, 23 °C, THF-d_8) δ −4.10 (s, 2H, Ru–*H*–Ru), 1.84 (s, 30H, Cp–*Me*), 7.1–8.0 (m, 10H, *Ph*). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, THF-d_8) δ 10.7 (Cp–*Me*), 88.5 (Cp-*ring*), 128.0 (*Ph*), 130.2 (*Ph*), 130.6 (*Ph*), 133.6 (*Ph*), 174.5 (Ph–*C*O–). IR (KBr, cm^{-1}): 2950, 2899, 1596, 1447, 1402, 1390, 1171, 1067, 1025, 995, 866, 852, 714, 706, 686, 476. Anal. Calcd for $C_{34}H_{42}O_4Ru_2$: C, 56.96; H, 5.91%. Found: C, 56.82; H, 5.90%.

Reaction of 1 with Acetic Acid. To a 50-mL Schlenk tube charged with [{Ru(C_5Me_5)}$_2$(μ-H)$_4$] (251 mg, 0.527 mmol) and tethahydrofuran (10 mL) was added CH_3CO_2H (5.0 mL, 87 mmol). After stirring for 36 h at room temperature, the mixture became red-orange and homogeneous. The solvent and excess acid were removed in vacuo. The resulting brown-red residue was extracted with diethyl ether (10 mL × 5) to leave [{Ru(C_5Me_5)}$_3$(μ-H)$_6$](CH_3CO_2) (**2e**) (71 mg, 26%) as a brown-purple solid. The resulting solution was filtered through a Celite pad, and dried in vacuo to afford [{Ru(C_5Me_5)}$_2$(μ-H)$_2$(μ-OCOCH_3)$_2$] (**3e**) (227 mg, 73%) as a red-orange solid. **2e**: ^{1}H NMR (270 MHz, 23 °C, CD_2Cl_2) δ −11.21 (s, 6H, Ru–*H*–Ru), 1.73 (s, 3H, CH_3CO_2), 1.98 (s, 45H, Cp–*Me*). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, CD_2Cl_2) δ 12.3 (Cp–*Me*), 22.3 (*C*H_3CO_2), 98.1 (Cp-*ring*), 175.3 (CH_3CO_2). IR (KBr, cm^{-1}): 1563 (ν_{CO}). Although this material appeared to be pure by ^{1}H NMR, several attempts to obtain satisfactory elemental analyses were unsuccessful because of its instability, even in the solid state. **3e**: ^{1}H NMR (270 MHz, 23 °C, THF-d_8) δ −4.41 (s, 2H, Ru–*H*–Ru), 1.69 (s, 30H, Cp–*Me*), 1.81 (s, 6H, CH_3CO_2). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, THF-d_8) δ 10.5 (Cp–*Me*), 22.0 (*C*H_3CO_2), 87.9 (Cp-*ring*), 178.5 (CH_3–*C*O–). IR (KBr, cm^{-1}): 2970, 2893, 1571, 1412, 1372, 1340, 1257, 1154, 1072, 1043, 990, 843, 710, 673, 618, 583, 431, 392. Anal. Calcd for $C_{24}H_{38}O_4Ru_2$: C, 48.64; H, 6.46%. Found: C, 48.70; H, 6.58%.

Reaction of 1 with Trifluoroacetic Acid. To a suspension of [{Ru(C_5Me_5)}$_2$(μ-H)$_4$] (344 mg, 0.72 mmol) in tetrahydrofuran (10 mL) was added CF_3CO_2H (2.16 M in THF) (0.67 mL, 1.45 mmol) at room temperature with vigorous stirring. After being stirred for 4 h at room temperature, the solvent was removed under reduced pressure from the reaction mixture. Extraction from the residual brown solid with diethyl ether (20 mL × 5) afforded [{Ru(C_5Me_5)}$_2$(μ-H)$_2$(μ-OCOCF_3)$_2$] (**3a**) (495 mg, 98%) as a red-orange crystalline solid. **3a**: ^{1}H NMR (270 MHz, 23 °C, $CDCl_3$) δ −4.50 (s, 2H, Ru–*H*–Ru), 1.72 (s, 30H, Cp–*Me*). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, $CDCl_3$) δ 10.4 (Cp–*Me*), 89.2 (Cp-*ring*), 113.7 (q, J_{CF} = 286.8 Hz, *C*F_3CO_2), 165.8 (q, $^2J_{CF}$ = 37.5 Hz, CF_3CO_2). T_1 (270 MHz, −50 °C, CD_2Cl_2): 251 ms. IR (KBr, cm^{-1}): 2910, 1656 (ν_{CO}), 1446, 1382, 1199, 1146, 1079, 1050, 993, 868, 858, 784, 732. Anal. Calcd for $C_{24}H_{32}F_6O_4Ru_2$: C, 41.14; H, 4.60%. Found: C, 41.34; H, 4.42%.

Reaction of 1 with Formic Acid. To a suspension of [{Ru(C_5Me_5)}$_2$(μ-H)$_4$] (180 mg, 0.38 mmol) in tetrahydrofuran (10 mL) was added formic acid (0.15 mL, 4.0 mmol) at room temperature with vigorous stirring. After being stirred for 1 h at room temperature, the solvent was removed under reduced pressure from the reaction mixture. Extraction from the residual brown solid with diethyl ether (10 mL × 3) afforded [{Ru(C_5Me_5)}$_2$(μ-H)$_2$(μ-OCOH)$_2$] (**3b**) (173 mg, 81%) as a red-orange crystalline solid. **3b**: ^{1}H NMR (270 MHz, 23 °C, THF-d_8) δ −4.40 (s, 2H, Ru–*H*–Ru), 1.72 (s, 30H, Cp–*Me*), 6.75 (s, 1H, –OCO*H*). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, THF-d_8) δ 10.6 (Cp–*Me*), 88.5 (Cp-*ring*), 170.4 (–*O*COH). IR (KBr, cm^{-1}): 2952, 2905, 2835, 1593 (ν_{CO}), 1463, 1374, 1360, 1344, 1264, 1078, 1026, 987, 846, 790, 587. Anal. Calcd for $C_{22}H_{34}O_4Ru_2$: C, 46.80; H, 6.07%. Found: C, 46.67; H, 6.13%.

Reaction of 1 with 1-Adamantanecarboxylic Acid. To a 50-mL Schlenk tube charged with [{Ru(C_5Me_5)}$_2$(μ-H)$_4$] (71 mg, 0.149 mmol) and 1-adamantanecarboxylic acid (54 mg, 0.300 mmol) was added tetrahydrofuran (10 mL). After stirring for 40 h at room temperature, the mixture became red-orange and homogeneous. The solvent and excess acid were removed in vacuo. Extraction from the resulting brown-red residue with diethyl ether (10 mL × 5) followed by removal of solvent under reduced pressure gave [{Ru(C_5Me_5)}$_2$(μ-H)$_2$(μ-OCO$C_{10}H_{15}$)$_2$] (**3c**) (110 mg, 89%) as a red-orange crystalline solid. **3c**: ^{1}H NMR (270 MHz, 23 °C, THF-d_8) δ −4.49 (s, 2H, Ru–*H*–Ru), 1.72 (s, 30H, Cp–*Me*), 1.6–1.7 (m, *adamantyl*), 1.8–1.9 (m, *adamantyl*). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, THF-d_8) δ 10.6 (Cp–*Me*), 29.8 (*adamantyl*), 37.9 (*adamantyl*), 41.7 (*adamantyl*), 87.9 (Cp-*ring*), 184.9 ($C_{10}H_{15}$–*C*OO). The resonance for the quarternary carbon of adamantyl group could not be observed. IR (KBr, cm^{-1}): 2893, 2843, 1562 (ν_{CO}), 1451, 1398, 1371, 1344, 1311, 1089, 993, 840, 764, 674. Anal. Calcd for $C_{42}H_{62}O_4Ru_2$: C, 60.55; H, 7.50%. Found: C, 60.26; H, 7.43%.

Reaction of 2c with $NaBPh_4$. To a stirred suspension of [{Ru(C_5Me_5)}$_3$(μ-H)$_6$] (1/2SO_4 + H_2SO_4) (100 mg, 0.116 mmol) in tetrahydrofuran (10 mL) was added $NaBPh_4$ (198 mg, 0.580 mmol) at 25 °C. After being stirred for 6 h at room temperature, the mixture was passed through a column packed with neu-

tral alumina. Removal of the solvent from the eluent under reduced pressure afforded $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](BPh_4)$ (**2f**) (118 mg, 99%) as a red-purple crystalline solid. Slow cooling of tetrahydrofuran solution of **2f** to −20 °C gave single crystals that included tetrahydrofuran as a solvent of crystallization. **2f**: ^{1}H NMR (500 MHz, 24 °C, THF-d_8) δ −11.28 (s, 6H, Ru–*H*–Ru), 1.93 (s, 45H, Cp–*Me*), 6.87 (t, $J = 7.5$ Hz, 4H, *Ph*), 7.03 (t, $J = 7.5$ Hz, 8H, *Ph*), 7.42 (m, 8H, *Ph*). ^{13}C NMR (125 MHz, 24 °C, THF-d_8) δ 12.1 (Cp–*Me*), 97.6 (Cp-*ring*), 121.5 (*Ph*), 125.4 (*Ph*), 136.4 (*Ph*), 164.4 (q, $J_{BC} = 49$ Hz, *Ph*). IR (KBr, cm^{-1}): 2988, 2910, 2866, 1580, 1460, 1428, 1378, 1068, 1024, 845, 734, 704, 640, 612, 534, 516, 482, 470, 429, 410. Anal. Calcd for $C_{54}H_{71}BRu_3 + C_4H_8O$: C, 62.97; H, 7.20%. Found: C, 62.99; H, 7.19%.

Reaction of 2c with NH_4PF_6. To a stirred suspension of $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](1/2SO_4 + H_2SO_4)$ (175 mg, 0.203 mmol) in tetrahydrofuran (15 mL) was added NH_4PF_6 (342 mg, 2.10 mmol) at 25 °C. After being stirred for 40 min at room temperature, the mixture was passed through a column packed with alumina. Removal of the solvent from the eluent under reduced pressure afforded $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6](PF_6)$ (**2g**) (123 mg, 70%) as an analytically pure red-purple crystalline solid. Slow cooling of a saturated dioxane/dimethoxyethane (1/1) solution of **2g** to 5 °C gave single crystals that included three dioxane molecules in a unit cell as a solvent of crystallization. **2g**: ^{1}H NMR (500 MHz, 24 °C, $CDCl_3$) δ −11.24 (s, 6H, Ru–*H*–Ru), 1.99 (s, 45H, Cp–*Me*). ^{13}C NMR (125 MHz, 24 °C, THF-d_8) δ 12.1 (Cp–*Me*), 97.8 (Cp-*ring*). IR (KBr, cm^{-1}): 2990, 2916, 1466, 1381, 1079, 1024, 875, 843, 798, 642, 613, 559, 536, 513, 467, 435, 406. Anal. Calcd for $C_{30}H_{51}F_6PRu_3$: C, 41.90; H, 5.98%. Found: C, 41.70; H, 6.49%.

Reaction of $[\{Ru(C_5Me_4Et)\}_2(\mu\text{-}H)_4]$ with Sulfuric Acid. To a suspension of $[\{Ru(C_5Me_4Et)\}_2(\mu\text{-}H)_4]$ (421 mg, 0.833 mmol) in tetrahydrofuran (20 mL) was added H_2SO_4 (0.20 M in Et_2O) (4.2 mL, 0.84 mmol) with vigorous stirring at room temperature. After being stirred for 12 h at room temperature, the solvent was removed under reduced pressure from the reaction mixture. Washing the residual solid with diethyl ether (20 mL × 5) afforded $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)_6](1/2SO_4 + H_2SO_4)$ (**2c′**) (467 mg, 93%) as a red-purple crystalline solid. Several attempts to obtain satisfactory elemental analyses were unsuccessful. **2c′**: ^{1}H NMR (300 MHz, 23 °C, $CDCl_3$) δ −11.25 (s, 6H, Ru–*H*–Ru), 1.12 (t, $J = 7.6$ Hz, 9H, Cp–CH_2–*Me*), 1.99 (s, 36H, Cp–*Me*), 2.32 (q, $J = 7.6$ Hz, 6H, Cp–C*H*$_2$–Me). ^{13}C NMR (75 MHz, 23 °C, $CDCl_3$) δ 11.9 (q, $J_{CH} = 128.5$ Hz, Cp–*Me*), 12.1 (q, $J_{CH} = 128.5$ Hz, Cp–*Me*), 14.8 (qt, $J_{CH} = 127.7$, 4.7 Hz, Cp–CH_2–*Me*), 20.2 (tq, $J_{CH} = 129.1$, 3.9 Hz, Cp–*C*H_2–Me), 97.1 (s, Cp-*ring*), 98.5 (s, Cp-*ring*), 102.6 (s, Cp-*ring*).

Reaction of 2c′ with $NaBPh_4$. To a stirred solution of $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)_6](1/2SO_4 + H_2SO_4)$ (320 mg, 0.355 mmol) in tetrahydrofuran (20 mL) was added $NaBPh_4$ (610 mg, 1.78 mmol) at room temperature. After stirring for 30 min at room temperature, the mixture was passed through a column packed with alumina. Removal of solvent from the eluent under reduced pressure gave $[\{Ru(C_5Me_4Et)\}_3(\mu\text{-}H)_6](BPh_4)$ (**2f′**) (345 mg, 90%) as a red-purple crystalline solid. Slow cooling of a saturated tetrahydrofuran/diethyl ether solution of **2f′** to −30 °C afforded red-purple single crystals. **2f′**: ^{1}H NMR (300 MHz, 23 °C, $CDCl_3$) δ −11.30 (s, 6H, Ru–*H*–Ru), 1.09 (t, $J = 7.6$ Hz, 9H, Cp–CH_2–*Me*), 1.90 (s, 18H, Cp–*Me*), 1.92 (s, 18H, Cp–*Me*), 2.27 (q, $J = 7.6$ Hz, 6H, Cp–C*H*$_2$–Me), 6.86 (t, $J = 7.1$ Hz, 4H, Ph-*para*), 7.03 (t, $J = 7.3$ Hz, 8H, Ph-*meta*), 7.42 (br, 8H, Ph-*ortho*). ^{13}C NMR (75 MHz, 23 °C, $CDCl_3$) δ 11.9 (q, $J_{CH} = 128.4$ Hz, Cp–*Me*), 12.1 (q, $J_{CH} = 128.5$ Hz, Cp–*Me*), 14.7 (qt, $J_{CH} = 127.8$, 4.3 Hz, Cp–CH_2–*Me*), 20.2 (tq, $J_{CH} = 129.1$, 4.1 Hz, Cp–*C*H_2–Me), 97.1 (s, Cp-*ring*), 98.4 (s, Cp-*ring*), 102.6 (s, Cp-*ring*), 121.7 (dt, $J_{CH} = 156.7$, 7.8 Hz, Ph-*para*), 125.6 (d, $J_{CH} = 153.0$ Hz, Ph-*meta*), 136.6 (dt, $J_{CH} = 154.1$, 7.3 Hz, Ph-*ortho*), 163.6 (s, Ph-*ipso*), 164.3 (s, Ph-*ipso*), 165.0 (s, Ph-*ipso*), 165.6 (s, Ph-*ipso*). IR (KBr, cm^{-1}): 3056, 3036, 2927, 2912, 2874, 1580, 1456, 1428, 1378, 1085, 1052, 1028, 844, 734, 702, 634, 613. Anal. Calcd for $C_{57}H_{77}BRu_3$: C, 63.61; H, 7.21%. Found: C, 63.87; H, 7.51%.

Reaction of 1 with Trifluoromethanesulfonic Acid in the Presence of Benzene. To a suspension of $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]$ (70 mg, 0.15 mmol) in a mixed solvent of tetrahydrofuran (5 mL) and benzene (2 mL) was added CF_3SO_3H (1.0 M in Et_2O) (0.5 mL, 0.5 mmol) at 25 °C with vigorous stirring. Immediately, the color of the solution changed from red to green-brown with the evolution of hydrogen. After being stirred for 1 h, the solution was allowed to stand. The colorless solid of $[Ru(C_5Me_5)(C_6H_6)](CF_3SO_3)$ (**4**) (133 mg, 97%) precipitated from the solution was collected on a glass frit. **4**: ^{1}H NMR (270 MHz, 23 °C, CD_3COCD_3) δ 2.04 (s, 15H, Cp–*Me*), 5.97 (s, 6H, C_6H_6). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, CD_3COCD_3) δ 9.74 (Cp–*Me*), 87.0 (C_6H_6), 96.5 (Cp-*ring*). IR (KBr, cm^{-1}): 3072, 2981, 2909, 1258, 1170, 1041, 645, 581, 528. FD-MS: m/z 316. Anal. Calcd for $C_{17}H_{21}F_3O_3SRu$: C, 44.07; H, 4.57%. Found: C, 43.96; H, 4.65%.

Reaction of 1 with Tetrafluoroboric Acid in the Presence of Acetonitrile. To a 50-mL Schlenk tube charged with acetonitrile (1 mL), diethyl ether (5 mL), methanol (5 mL), and HBF_4 (85 wt % in Et_2O) (75 μL), a solution of $[\{Ru(C_5Me_5)\}_2(\mu\text{-}H)_4]$ (126 mg, 0.27 mmol) in diethyl ether (10 mL) was slowly added through a dropping funnel at 25 °C with vigorous stirring. After being stirred for 1 h at ambient temperature, the solvent was removed under reduced pressure from the reaction mixture; washing the residual yellow crystalline solid with diethyl ether (5 mL × 5) yielded $[Ru(C_5Me_5)(CH_3CN)_3](BF_4)$ (**5**) (410 mg, 98%). **5**: ^{1}H NMR (300 MHz, 23 °C, CD_3COCD_3) δ 1.61 (s, 15H, Cp–*Me*), 2.37 (s, 9H, C*H*$_3$CN). Anal. Calcd for $C_{16}H_{24}N_3BF_4Ru$: C, 43.06; H, 5.42; N, 9.42%. Found: C, 43.23; H, 5.33; N, 9.56%.

Determination of Equilibrium Constant among 2d, 6, and Benzoic Acid. Benzoic acid (112 mg, 0.92 mmol) and $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ (**6**) (30 mg, 0.042 mmol) were dissolved in tetrahydrofuran-d_8 (0.60 mL). After the solution was charged in an NMR tube, the tube was sealed. The equilibrium constant K, where $K = [\mathbf{2d}]/([\mathbf{6}][PhCO_2H])$, was determined based on ^{1}H NMR integration of the hydride signals for **2d** and **6**. The constant K was 0.76, 0.47, 0.36, 0.31, 0.27, 0.21, 0.19, and 0.14 [M^{-1}] at 293, 303, 308, 313, 318, 323, 328, and 333 K, respectively.

Preparation of $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ (6). To a stirred solution of $[\{Ru(C_5Me_5)\}_3(\mu\text{-}H)_6]\cdot 1/2(SO_4 + H_2SO_4)$ (1.211 g, 1.405 mmol) in methanol (30 mL) was added CH_3ONa (302 mg, 5.60 mmol) at 25 °C. After being stirred for 10 min, the solvent was removed under reduced pressure. A black-brown residue was extracted with tetrahydrofuran (30 mL × 3), filtered through a column packed with alumina and the volatile material was removed to give **6** (964 mg, 96%) as a black-brown solid. **6**: ^{1}H NMR (500 MHz, 24 °C, C_6D_6) δ −7.22 (s, 5H, Ru–*H*–Ru), 2.04 (s, 45H, Cp–*Me*). ^{13}C NMR (125 MHz, 24 °C, C_6D_6) δ 13.1 (q, $J_{CH} = 126.2$ Hz, Cp–*Me*), 85.7 (s, Cp-*ring*). T_1 (500 MHz, THF-d_8): 8.63 s (at 20 °C), 4.33 s (at −50 °C), and 2.55

s (at −80 °C). Anal. Calcd for $C_{30}H_{50}Ru_3$: C, 50.47; H, 7.06%. Found: C, 50.27; H, 7.02%.

Preparation of [{Ru(C$_5$Me$_4$Et)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6′). To a stirred solution of [{Ru(C$_5$Me$_4$Et)}$_3$(μ-H)$_6$](BPh$_4$) (248 mg, 0.231 mmol) in methanol (10 mL) was added CH_3ONa (46 mg, 0.852 mmol) dissolved in 5 mL of methanol at room temperature. After stirring for 15 min at room temperature, the solvent was removed in vacuo. A black-brown residue was extracted with tetrahydrofuran (10 mL × 3) and filtered through a column packed with alumina. Removal of the solvent from the eluent to dryness gave **6′** (162 mg, 93%) as a red-brown crystalline solid. **6′**: ^{1}H NMR (500 MHz, 24 °C, C_6D_6) δ −7.13 (s, 5H, Ru–*H*–Ru), 1.07 (t, J = 7.5 Hz, 9H, Cp–CH$_2$–*Me*), 2.03 (s, 18H, Cp–*Me*), 2.10 (s, 18H, Cp–*Me*), 2.53 (q, J = 7.5 Hz, 6H, Cp–C*H*$_2$–Me). ^{13}C NMR (125 MHz, 24 °C, C_6D_6) δ 13.1 (q, J_{CH} = 126.4 Hz, Cp–*Me*), 13.2 (q, J_{CH} = 126.4 Hz, Cp–*Me*), 15.9 (qt, J_{CH} = 126.2, 4.3 Hz, Cp–CH$_2$–*Me*), 21.5 (tq, J_{CH} = 127.5, 4.3 Hz, Cp–*C*H$_2$–Me), 85.5 (s, Cp-*ring*), 86.4 (s, Cp-*ring*), 91.9 (s, Cp-*ring*). Anal. Calcd for $C_{33}H_{56}Ru_3$: C, 52.43; H, 7.47%. Found: C, 52.07; H, 7.15%.

H/D Exchange between [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6) and Benzene-d_6, Toluene-d_8, or *o*-Xylene-d_{10}. An NMR sample tube (5 ϕ), in which the atmosphere was replaced with argon, was charged with 6.0 mg (0.0084 mmol) of **6** and 0.62 mL of benzene-d_6. The tube was sealed after the solution was frozen by using a dry ice–methanol bath. The solution was then heated at 80 °C, and the ^{1}H NMR spectra were recorded at appropriate time intervals. In a similar manner, NMR samples were prepared using toluene-d_8 and *o*-xylene-d_{10} as solvents; the spectra were recorded at 80 °C.

Reaction of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6) with Benzene. Preparation of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-C$_6$H$_6$)] (7): A 50-mL glass autoclave, in which the atmosphere was replaced with argon, was charged with 36.8 mg (0.052 mmol) of **6** and 5 mL of benzene. The mixture was heated at 140 °C for 17 h. The color of the solution changed from brown to red-purple. After removal of the solvent under reduced pressure, the residual dark-purple microcrystalline solid was washed three times with methanol. Drying in vacuo gave **7** as a dark-purple crystalline solid (39.6 mg, 97%). The product was identified by a comparison of its ^{1}H NMR spectrum with that of authentic sample.

Reaction of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6) with Trimethylphosphine. Preparation of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_5$-{P(CH$_3$)$_3$}] (8a): To a 50-mL Schlenk tube charged with 285 mg (0.400 mmol) of **6** and tetrahydrofuran (10 mL) was added 0.51 mL (0.800 mmol) of a solution of trimethylphosphine in toluene (1.57 M) at room temperature. The color of the reaction mixture immediately turned from dark-red to purple. After being stirred for 10 min at ambient temperature, the solvent was removed under reduced pressure from the reaction mixture to yield **8a** (300 mg, 95%). The slow cooling of a saturated tetrahydrofuran solution of **8a** to −30 °C afforded purple prisms suitable for an X-ray diffraction study. **8a**: ^{1}H NMR (300 MHz, 24 °C, C_6D_6) δ −11.82 (d, J_{PH} = 10.9 Hz, 5H, Ru–*H*–Ru), 1.06 (d, J_{PH} = 8.3 Hz, 9H, P–*Me*), 1.87 (d, J_{PH} = 1.8 Hz, 15H, Cp–*Me*), 2.02 (s, 30H, Cp–*Me*). ^{1}H NMR (500 MHz, −108 °C, tetrahydrofuran-d_8/toluene-d_8) δ −23.50 (s, 1H, Ru–*H*–Ru), −11.06 (s, 1H, Ru–*H*–Ru), −10.90 (d, J_{PH} = 32.5 Hz, 2H, Ru–*H*–Ru), −2.96 (s, 1H, Ru–*H*–Ru), 1.06 (d, J_{PH} = 8.3 Hz, 9H, P–*Me*), 1.87 (d, J_{PH} = 1.8 Hz, 15H, Cp–*Me*), 2.02 (s, 30H, Cp–*Me*). ^{13}C NMR (75.5 MHz, 24 °C, C_6D_6) δ 12.3 (q, J_{CH} = 126 Hz, Cp–*Me*), 13.4 (q, J_{CH} = 126 Hz, Cp–*Me*), 24.5 (dq, J_{PC} = 27.6 Hz, J_{CH} = 126 Hz, P–*Me*), 82.9 (s, Cp-*ring*), 90.0 (d, J_{PC} = 2.6 Hz, Cp-*ring*). ^{31}P{^{1}H} NMR (109.4 MHz, 24 °C, C_6D_6–H_3PO_4) δ 12.0. Anal. Calcd for $C_{33}H_{59}PRu_3$: C, 50.17; H, 7.53%. Found: C, 49.79; H, 7.52%.

Reaction of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6) with Triphenyl Phosphite. Preparation of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_5$-{P(OC$_6$H$_5$)$_3$}] (8b): To a 50-mL Schlenk tube charged with 133 mg (0.186 mmol) of **6** and tetrahydrofuran (2.8 mL) was added triphenyl phosphite (98.0 μL, 0.370 mmol) at room temperature. The color of the reaction mixture immediately turned from dark-red to red-purple. Removal of the solvent under reduced pressure, followed by crystallization from tetrahydrofuran at −30 °C, afforded **8b** (171 mg, 82%). The slow cooling of saturated tetrahydrofuran solution of **8b** to −30 °C afforded red-purple prisms suitable for an X-ray diffraction study. **8b**: ^{1}H NMR (300 MHz, 24 °C, C_6D_6) δ −11.13 (d, J_{PH} = 10.3 Hz, 5H, Ru–*H*–Ru), 1.83 (d, J_{PH} = 1.8 Hz, 15H, Cp–*Me*), 2.06 (s, 30H, Cp–*Me*), 6.84 (t, J = 7 Hz, 3H, *para*), 7.08 (t, J = 7 Hz, 6H, *meta*), 7.24 (t, J = 7 Hz, 6H, *ortho*). ^{13}C NMR (75.5 MHz, 24 °C, C_6D_6) δ 12.4 (q, J_{CH} = 127 Hz, Cp–*Me*), 13.0 (q, J_{CH} = 127 Hz, Cp–*Me*), 85.7 (s, Cp-*ring*), 92.6 (d, J_{PC} = 4.1 Hz, Cp-*ring*), 121.6 (dddd, J = 162.8, 7.3, 4.0, 4.0 Hz, *ortho*), 122.6 (dt, J = 162.2, 7.1 Hz, *para*), 128.8 (dd, J = 161.6, 8.3 Hz, *meta*), xxx.x (dt, J = 13.0, 9 Hz, *ipso*). ^{31}P{^{1}H} NMR (109.4 MHz, 24 °C, C_6D_6–H_3PO_4) δ 134. Anal. Calcd for $C_{55}H_{73}O_3PRu_3$: C, 58.80; H, 6.70%. Found: C, 59.17; H, 6.59%.

Reaction of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6) with Dioxygen. Preparation of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-O)] (9): A 50-mL Schlenk tube was charged with 93 mg (0.13 mmol) of **6**, 7 mL of tetrahydrofuran, and 0.3 mL of methanol. The Schlenk tube was evacuated with cooling at −78 °C. Then, 1.1 equiv (0.14 mmol) of dioxygen dried over P_2O_5 was admitted to the reactor by use of a vacuum line. The mixture was stirred for 1.5 h under the temperature range from −78 to −60 °C. The color changed from dark-brown to black-green. Immediately after removal of the cooling bath, the solvent was removed in vacuo to afford an 88/12 mixture of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-O)] (**9**) and [{Ru(C$_5$Me$_5$)}$_3$(μ-H)(μ_3-O)$_2$] (**10**) as a black-green solid (94 mg) in a quantitative yield. Slow cooling of a tetrahydrofuran solution of the resulting mixture to −30 °C gave analytically pure **9** as black-green crystals. **9**: ^{1}H NMR (300 MHz, 23 °C, C_6D_6) δ −11.51 (s, 3H, Ru–*H*–Ru), 1.80 (s, 45H, Cp–*Me*). ^{13}C NMR (75 MHz, 23 °C, C_6D_6) δ 12.5 (q, J_{CH} = 126.6 Hz, Cp–*Me*), 92.0 (s, Cp-*ring*). Anal. Calcd for $C_{30}H_{48}ORu_3$: C, 49.50; H, 6.65%. Found: C, 49.12; H, 6.72%.

Reaction of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6) with Dioxygen. Preparation of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)(μ_3-O)$_2$] (10): A 50-mL Schlenk tube was charged with 100 mg (0.140 mmol) of **6**, 10 mL of tetrahydrofuran, and 2 mL of methanol. The solution was cooled to −78 °C and the Schlenk tube was evacuated. Then, 2 equiv (0.29 mmol) of dioxygen dried over P_2O_5 was admitted to the reactor by using a vacuum line. The mixture was stirred for 50 min at −50 °C and for 10 min at 0 °C. The resulting mixture was passed through a column packed with alumina, and the solvent was removed in vacuo to give [{Ru(C$_5$Me$_5$)}$_3$(μ-H)(μ_3-O)$_2$] (**10**) as a brown solid. The slow cooling of a tetrahydrofuran-diethyl ether solution of **10** to −30 °C gave analytically pure **10+H$_2$O** (84.8 mg, 80%) as black-brown needles. **10**: ^{1}H NMR (300 MHz, 23 °C, C_6D_6) δ −15.84 (s, 1H, Ru–*H*–Ru), 1.76 (s, 30H, Cp–*Me*), 1.78 (s, 15H, Cp–*Me*). ^{13}C{^{1}H} NMR (75 MHz, 23 °C, C_6D_6) δ 11.8 (Cp–*Me*), 12.2 (Cp–*Me*), 90.9 (Cp-*ring*), 91.3 (Cp-*ring*). IR (KBr, cm^{-1}): 2984, 2960, 2906,

2858, 1431, 1404, 1377, 1079, 1067, 1027. Anal. Calcd for $C_{30}H_{46}O_2Ru_3 + H_2O$: C, 47.41; H, 6.36%. Found: C, 47.44; H, 6.42%.

Reaction of [{Ru(C$_5$Me$_4$Et)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6′) with Dioxygen. Preparation of [{Ru(C$_5$Me$_4$Et)}$_3$(μ-H)(μ_3-O)$_2$] (10′): A 50-mL Schlenk tube was charged with 115 mg (0.152 mmol) of **6′**, 10 mL of tetrahydrofuran, and 2 mL of methanol. The mixture was cooled to −78 °C. After the Schlenk tube was evacuated, 2 equiv of dioxygen dried over P_2O_5 was admitted to the tube by using a vacuum line. The mixture was stirred for 30 min at room temperature. The resulting mixture was passed through a column packed with alumina. Removal of the solvent under reduced pressure gave **10′+H$_2$O** (112 mg, 92%) as a yellow-brown crystalline solid. Recrystallization from the mixed solvent of tetrahydrofuran and diethyl ether at −20 °C gave single crystals of **10′** as black-brown needles. **10′**: ^{1}H NMR (300 MHz, 23 °C, C_6D_6) δ −15.82 (s, 1H, Ru–*H*–Ru), 1.05 (t, $J = 7.6$ Hz, 6H, Cp–CH$_2$–*Me*), 1.16 (t, $J = 7.6$ Hz, 3H, Cp–CH$_2$–*Me*), 1.75 (s, 12H, Cp–*Me*), 1.79 (s, 6H, Cp–*Me*), 1.808 (s, 12H, Cp–*Me*), 1.813 (s, 6H, Cp–*Me*), 2.18 (q, $J = 7.6$ Hz, 2H, Cp–C*H*$_2$–Me), 2.22 (q, $J = 7.6$ Hz, 4H, Cp–C*H*$_2$–Me). ^{13}C NMR (75 MHz, 23 °C, C_6D_6) δ 11.98 (q, $J = 126.7$ Hz, Cp–*Me*), 12.04 (q, $J = 126.7$ Hz, Cp–*Me*), 12.4 (q, $J = 126.4$ Hz, Cp–*Me*), 12.5 (q, $J = 126.4$ Hz, Cp–*Me*), 15.6 (tq, $J = 4.4$, 126.4 Hz, Cp–CH$_2$–*Me*), 15.7 (tq, $J = 4.4$, 126.4 Hz, Cp–CH$_2$–*Me*), 20.6 (qt, $J = 4.4$, 127.4 Hz, Cp–*C*H$_2$–Me), 21.0 (qt, $J = 4.4$, 127.2 Hz, Cp–*C*H$_2$–Me), 90.4 (s, Cp-*ring*), 90.9 (s, Cp-*ring*), 91.3 (s, Cp-*ring*), 91.6 (s, Cp-*ring*), 97.0 (s, Cp-*ring*), 97.2 (s, Cp-*ring*). IR (KBr, cm^{-1}): 3550, 3420, 2966, 2900, 2104, 1648, 1562, 1456, 1408, 1377, 1307, 1262, 1155, 1082, 1020, 963, 829, 670, 633, 526. Anal. Calcd for $C_{33}H_{52}O_2Ru_3 + H_2O$: C, 49.42; H, 6.79%. Found: C, 49.02; H, 6.98%.

Reaction of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6) with Iodomethane. Preparation of [{Ru(C$_5$Me$_5$)}$_3$(μ_3-H)(μ-H)$_3$(μ_3-I)] (11): To a stirred solution of **6** (253 mg, 0.355 mmol) in 20 mL of tetrahydrofuran was added iodomethane (26 mg, 0.382 mmol) at 25 °C. After being stirred for 24 h at room temperature, the resulting solution was filtered through a Celite pad, and dried in vacuo to afford [{Ru(C$_5$Me$_5$)}$_3$(μ_3-I)(μ_3-H)(μ-H)$_3$] (**11**) as a black-brown solid (275 mg, 92%). The slow cooling of a saturated tetrahydrofuran–pentane solution of 6 to −20 °C gave single crystals of **11** as black-brown needles. **11**: ^{1}H NMR (270 MHz, 23 °C, C_6D_6) δ −2.25 (s, 4H, Ru–*H*), 2.12 (s, 45H, Cp–*Me*). ^{13}C{^{1}H} NMR (67.5 MHz, 23 °C, $CDCl_3$) δ 13.2 (q, $J = 126.7$ Hz, Cp–*Me*), 84.5 (s, Cp-*ring*). IR (KBr, cm^{-1}): 2962, 2888, 1448, 1369, 1146, 1067, 1020, 608, 580, 497, 432. Anal. Calcd for $C_{30}H_{49}IRu_3$: C, 42.90; H, 5.88; I, 15.11%. Found: C, 42.71; H, 5.74; I, 15.17%.

Monitoring the Reaction of 6 with Iodomethane in Tetrahydrofuran-d_8. A ^{1}H NMR sample tube was charged with **6** (14.3 mg, 20 μmol) and tetrahydrofuran-d_8 (0.5 mL). Iodomethane (1.1 μL, 0.18 μmol) was then added to the cooled (−30 °C) solution, and the tube was sealed. Spectra were recorded at appropriate time intervals. ^{1}H NMR (300 MHz, 23 °C, THF-d_8) δ −2.38 (s, 4H, Ru–*H*), 2.06 (s, 45H, Cp–*Me*), 0.19 (s, C*H*$_4$).

Reaction of [{Ru(C$_5$Me$_5$)}$_3$(μ-H)$_3$(μ_3-H)$_2$] (6) with Carbon Monoxide. Preparation of [{Ru(C$_5$Me$_5$)}$_3$(μ-CO)$_3$(μ_3-CO)] (12): A 50-mL Schlenk tube, equipped with a rubber balloon filled with CO, was charged with 214 mg (0.30 mmol) of **6** and 10 mL of tetrahydrofuran. The mixture was then cooled to −78 °C. After the Schlenk tube was evacuated, carbon monoxide was admitted to the tube. The resulting mixture was stirred for 12 h at room temperature, and was then passed through a column packed with Celite. Removal of the solvent from the eluent under reduced pressure gave **12** (209 mg, 85%) as a green-black solid. Slow cooling of a tetrahydrofuran solution of **12** to −34 °C afforded green-black single crystals. **12**: IR (KBr, cm^{-1}): 2944, 2888, 2821, 1782, 1735, 1615, 1473, 1447, 1422, 1370, 1068, 1022, 515. Anal. Calcd for $C_{34}H_{45}O_4Ru_3$: C, 49.74; H, 5.53%. Found: C, 49.67; H, 5.43%. FD-MS: 813 (8), 814 (16), 815 (20), 816 (33), 817 (45), 818 (59), 819 (78), 820 (88), 821 (95), 822 (199), 823 (83), 824 (70), 825 (55), 826 (28), 827 (22), 828 (10).

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