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Redox-Induced Reversible Rearrangement of a Dimetallaallyl Ligand on the Trinuclear Cluster of Ruthenium. Mechanistic Aspects of Formation of the Face-Capping μ_3-C$_3$ Ring on the Triruthenium Plane

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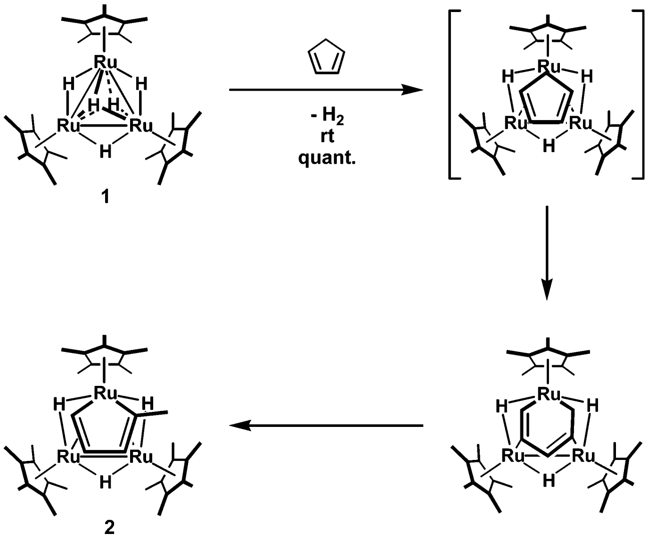
The dicationic complexes $[(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)(\mu\text{-}H)]^{2+}$ (**7a**,**b**; Cp* = η^5-C$_5$Me$_5$), containing a μ_3-η^3-C$_3$ ring on the Ru$_3$ triangle, were obtained by the reaction of a μ_3-methylidyne μ_3-η^1:η^3:η^1-2-methyldiruthenaallyl complex, $(Cp^*Ru)_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CHCMeCH)(\mu_3\text{-}CH)$ (**5a**), with 2 equiv of ferrocenium salt. The μ_3-η^3-C$_3$ ring was structurally characterized for the monocationic complex $[(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)]^+$ (**8**), which was obtained by deprotonation of a mixture of the regioisomers **7a**,**b**. The carbenic character of the carbons in the μ_3-η^3-C$_3$ ring was shown in the unusually long C−C bond distances and J_{C-H} values. CV analysis of **5a** strongly indicates that transformation of the dimetallaallyl moiety to the μ_3-C$_3$ ring occurred on the dicationic Ru$_3$ centers, as well as isolation of a paramagnetic intermediate, $[(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CHCMeCH)(\mu\text{-}H)]^+$ (**6**), containing a μ_3-diruthenaallyl ligand.

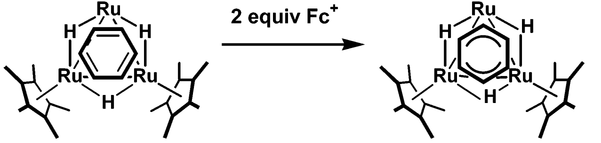
Introduction

Cooperative interaction of the multiple metal centers of the cluster has been shown to direct notable skeletal rearrangement reactions of the hydrocarbyls.[1] For example, an unactivated C−C bond of cyclopentadiene was readily cleaved in the triangle reaction field of the triruthenium pentahydrido complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**; Cp* = η^5-C$_5$Me$_5$) at ambient temperature, and a *nido*-ruthenacyclopentadiene complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}CMe{=}CHCH{=}CH{-})$ (**2**), was exclusively obtained (Scheme 1).[2] In this reaction, DFT calculations have shown[3] that μ_3-η^2:η^2 coordination of the cyclopentadiene is a key step in the C−C bond scission, and these calculations also demonstrate that the C−C bond was effectively activated by the multiple coordination on the cluster.

A cluster complex plays the role of a reservoir for holding electrons and, as a result, a multistep redox reaction would be possible between the cluster and the substrate. Reduction and oxidation of the metal sometimes result in the skeletal rearrangement of the hydrocarbyls on the cluster, since the electronic perturbation at the metal centers would be compensated by the change in the coordination mode of the ligand.[4] We have reported a hapticity change in the oxidation of a μ_3-η^2:η^2:η^2-benzene complex:[5] two-electron oxidation of $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ afforded $[\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^3{:}\eta^3\text{-}C_6H_6)]^{2+}$ as a consequence of rotation of the μ_3-benzene ligand by 30° on the Ru$_3$ plane (eq 1). Transformation of the alkyne ligand from perpendicular to parallel coordination upon reduction has been also well documented for the trimetallic complexes.[6]

Scheme 1





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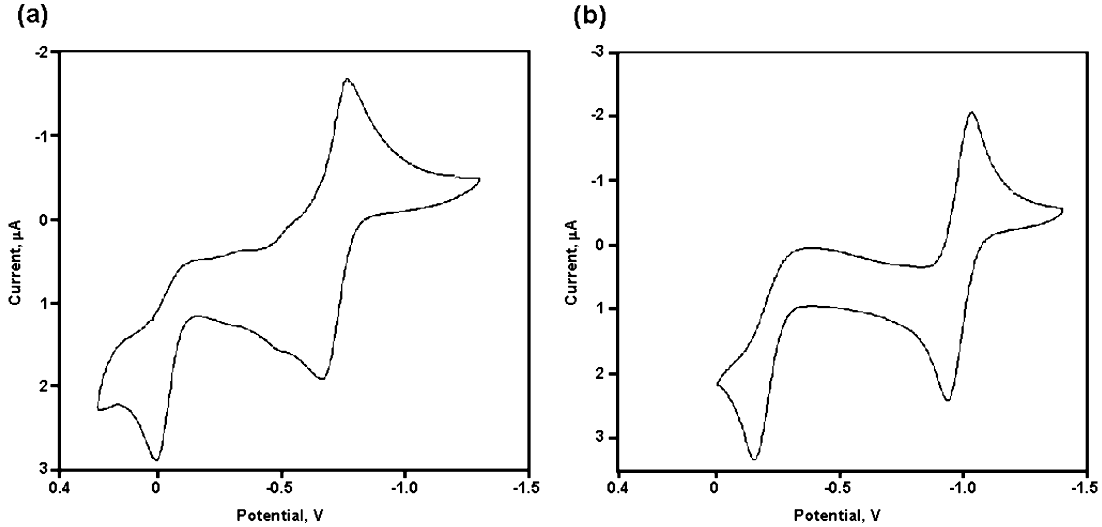
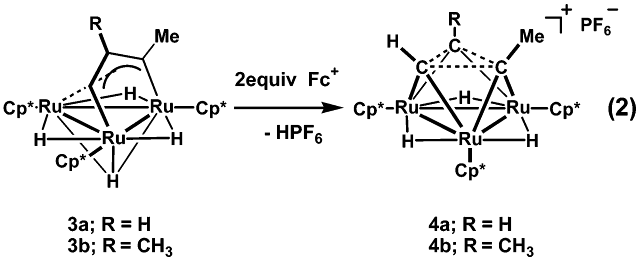
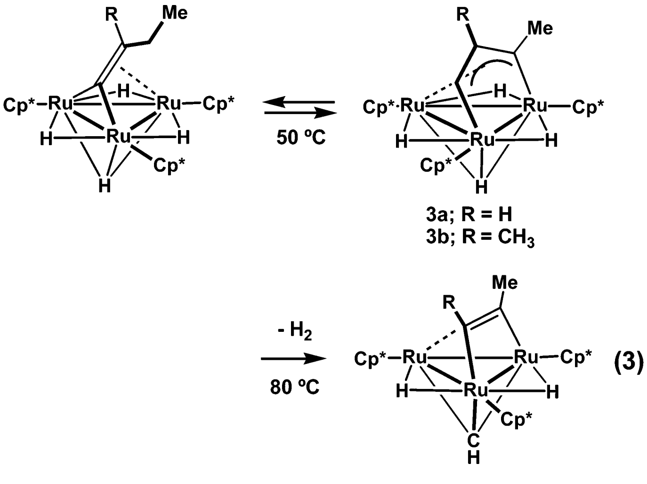


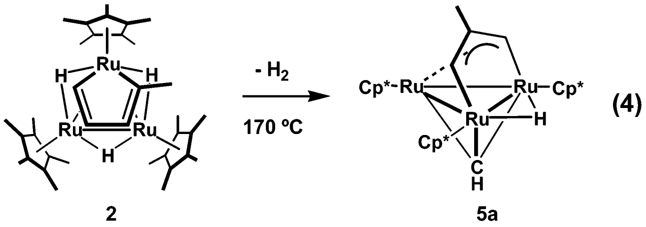
Figure 1. Cyclic voltammograms of (a) **5a** (0.5 mM) and (b) **3a** (1.0 mM) in THF at 25 °C. Conditions: electrolyte, 0.1 M $[NBu_4](PF_6)$; working electrode, Pt; scan rate, 50 mV/s. Potentials are referenced to Fc/Fc^+.

We have recently reported a novel type of skeletal rearrangement of the C_3 moiety of a μ_3-η^1:η^3:η^1-diruthenaallyl complex, $(Cp^*Ru)_3(\mu\text{-}H)_4(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-CHCRCMe})$ (**3a**, R = H; **3b**, R = Me),[7] promoted by chemical oxidation.[8] Treatment of **3** with 2 equiv of the hexafluorophosphate salt of the ferrocenium cation, $[Cp_2Fe]^+$ (Fc^+; Cp = η^5-C_5H_5), resulted in the exclusive formation of a hexafluorophosphate salt of the monocationic complex $[\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^3\text{-}C_3HRMe)]^+$ (**4**), which possessed a μ_3-η^3-C_3 ring on the Ru_3 plane (eq 2). This result is quite different from the thermal reaction of **3** (eq 3).[9] The μ_3-diruthenaallyl complex **3** equilibrated with a μ_3-vinylidene complex at 50 °C, and it underwent C−C bond cleavage to yield a μ_3-methylidyne-μ_3-η^2(||)-alkyne complex at 80 °C.





The formation of the μ_3-η^3-C_3 ring likely proceeds via a sequence of reactions, namely, two steps of one-electron oxidation, deprotonation, and C−C bond formation. In order to elucidate the mechanistic detail of the μ_3-C_3 ring formation, we investigated oxidation of the μ_3-methylidyne μ_3-η^1:η^3:η^1-diruthenaallyl complex $(Cp^*Ru)_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-CHCMeCH})(\mu_3\text{-CH})$ (**5a**), which was obtained by the thermolysis of the *nido*-ruthenacyclopentadiene complex **2** (eq 4).[10] Since **5a** contains a μ_3-methylidyne ligand, the redox potentials of **5a** were considerably different from those of **3** and enabled us to isolate several important intermediates of this skeletal rearrangement. We report herein the oxidation of the μ_3-η^1:η^3:η^1-diruthenaallyl complex **5a** and reactivity of a dicationic complex having a μ_3-C_3 ring.



Results and Discussion

One-Electron Oxidation of the μ_3-Methylidyne μ_3-η^1:η^3:η^1-2-Methyldiruthenaallyl Complex 5a. In order to assess the influence of the μ_3-methylidyne ligand, a solution of **5a** was subjected to a CV scan. The cyclic voltammogram of **5a** is depicted in Figure 1a, which showed reversible and irreversible one-electron waves. The reversible wave at $E_{1/2} = -718$ mV indicates the formation of a chemically stable 47-electron species. The second anodic peak was observed at $E_{p,a} = +5.70$ mV, but the corresponding cathodic peak was diminished, which implies that the second process is irreversible.

There have been only two reports so far on the electrochemical behavior of a triruthenium carbonyl cluster having a μ_3-

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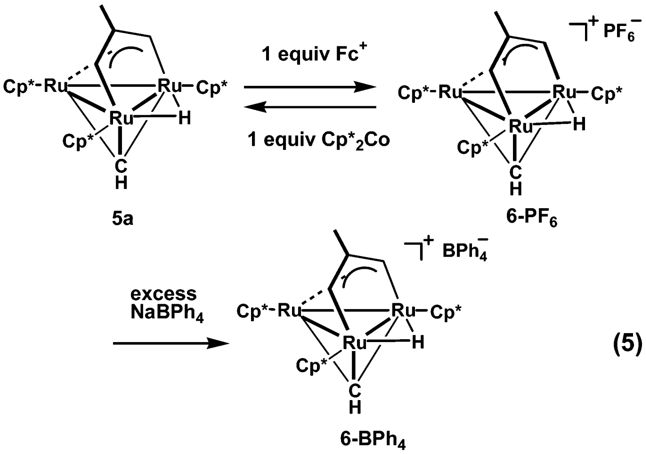
(10) Inagaki, A.; Takao, T.; Moriya, M.; Suzuki, H. *Organometallics* **2003**, *22*, 2196−2198.

diruthenaallyl ligand.[11] Keister and co-workers found two steps of one-electron-oxidation processes for the series of triruthenium complexes $Ru_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-XCCRCR}')(\mu\text{-H})$ (n = 0−3; X = OMe, NMe_2; R = Me, H; R′ = Me, OEt), and they noted that the first oxidation process was reversible to quasi-reversible and the second oxidation was irreversible.[11b] These redox peaks of the carbonyl clusters appeared at a considerably positive region in comparison with those found for **5a** and **3a**. For example, the $E_{1/2}$ and $E_{p,a}$ values of the triruthenium complex $Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-MeOCCMeCMe})(\mu\text{-H})$ were reported to be 0.27 and 0.74 V, respectively (referenced to Fc/Fc^+).[11b] In this study, it has been also noted that both π-donor substituents on the diruthenaallyl moiety and σ-donor substituents on the metal center lower the oxidation potentials. Therefore, lowering of the oxidation potentials of **5a** and **3a** was most likely due to both electron-rich metal centers stemming from the three Cp* ligands and the lack of electron-withdrawing carbonyl ligands.

While two redox waves were found in the cyclic voltammogram of **5a**, as found in that of the diruthenaallyl tetrahydrido complex **3a** (Figure 1b), both peaks considerably shift toward the positive direction; $E_{1/2}$ of the first reversible wave shifted by +0.27 V, and $E_{p,a}$ of the second irreversible wave also underwent a positive shift by +0.15 V. This shows that oxidation of the metal centers becomes difficult when the μ_3-methylidyne ligand is introduced. The μ_3-methylidyne ligand probably contributes to stabilizing the HOMO of **5a**.

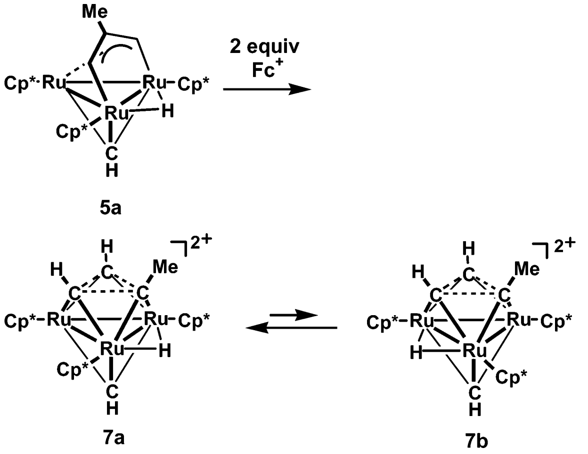
The reaction of **3a** with an equimolar amount of Fc^+ yielded **4a** as a major product instead of the intermediary 47e species anticipated from the CV analysis shown in Figure 1b. In contrast, treatment of **5a** with an equimolar amount of Fc^+ resulted in the exclusive formation of a hexafluorophosphate salt of the paramagnetic complex $[(Cp^*Ru)_3(\mu_3\text{-CH})(\mu_3\text{-CHCMeCH})(\mu\text{-H})]^+$ (**6**) (eq 5). This is probably due to the shift of the oxidation potentials toward the positive direction, which caused a considerable decrease of the rate of the second oxidation. Keister and co-workers detected the one-electron-oxidation products of the triruthenium carbonyl clusters $Ru_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-Me}_2\text{NCCHCMe})(\mu\text{-H})$ and $Ru_3(CO)_{9-n}(PPh_3)_n\{\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-MeOCCHC(OEt)}\}(\mu\text{-H})$ (n = 2, 3), by means of the EPR spectroscopy below −40 °C.[11b] On the basis of the reversibility of the redox wave of the carbonyl clusters, the paramagnetic species adopted a structure similar to that of the neutral species, but the researchers did not mention the structure of the paramagnetic species, due to the instability of the compounds.



(5)

The ^{1}H NMR spectra of a tetraphenylborate salt of **6,** which was obtained by the reaction of **6** with excess $NaBPh_4$, showed a broad signal at δ 43.68 ($w_{1/2}$ = 2120 Hz). This implied the formation of a paramagnetic 47e species. Since a single crystal suitable for the diffraction studies has not been obtained, structure determination of **6** has not been performed yet. However, quantitative reproduction of **5a** by one-electron reduction using Cp^*_2Co strongly supported that the skeletal rearrangement did not occur at this step, which is quite consistent with the reversibility of the first redox wave in the cyclic voltammogram. Therefore, it is concluded that complex **6** is a monocationic μ_3-methylidyne $\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1$-2-methyldiruthenaallyl complex, as shown in eq 5.

Two-Electron Oxidation of the μ_3-Methylidyne $\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1$-2-Methyldiruthenaallyl Complex 5a. Treatment of **5a** with 2 equiv of Fc^+ or further oxidation of the monocationic complex **6** by using an equimolar amount of Fc^+ in THF afforded a mixture of hexafluorophosphate salts of the dicationic complexes $[(Cp^*Ru)_3(\mu_3\text{-CH})(\mu_3\text{-}\eta^3\text{-C}_3\text{H}_2\text{Me})(\mu\text{-H})]^{2+}$ (**7a**,**b**) as a red precipitate (eq 6). These dicationic complexes were soluble in acetone and CH_2Cl_2, while they were sparingly soluble in THF and MeOH. Since complexes **7a**,**b** were in equilibrium in solution, only the averaged ^{1}H NMR spectrum was obtained at room temperature. Therefore, we characterized them on the basis of the ^{1}H and ^{13}C NMR spectra recorded at −70 °C. The molecular ratio between **7a** and **7b** was estimated as 67:33 at −70 °C.



(6)

The signals of the ring carbons of the major isomer **7a** were observed at δ 171.8 (d, J_{C-H} = 196.9 Hz, −*C*H) and 132.1 (s, −*C*Me) in the ^{13}C NMR spectra. The J_{C-H} value of 196.9 Hz is comparable to those of the structurally well-defined complexes containing a $\mu_3\text{-}\eta^3\text{-C}_3$ ring; the J_{C-H} values of the $\mu_3\text{-}\eta^3\text{-C}_3$ ring were 184.7 and 177 Hz for $[\{Cp^*Ru(\mu\text{-H})\}_3(\mu_3\text{-}\eta^3\text{-C}_3\text{H}_2\text{Me})]^+$ (**4a**)[8] and $(Cp^*Ru)_3(\mu_3\text{-}\eta^3\text{-C}_3\text{H}_2\text{Me})(\mu_3\text{-CO})$,[12] respectively. These values are considerably larger than the J_{C-H} values of the μ_3-dimetallaallyl ligand (J_{C-H} = 135.3−154.0 and 146.4−158.3 Hz for the terminal (C^1 and C^3) and the central (C^2) carbons, respectively).[7,10,13] Formation of the face-capping $\mu_3\text{-}\eta^3\text{-C}_3$ ring was confirmed by the X-ray diffraction study for a tetraphenylborate salt of $[(Cp^*Ru)_3(\mu_3\text{-CH})(\mu_3\text{-}\eta^3\text{-C}_3\text{H}_2\text{Me})]^+$ (**8**), which was obtained by deprotonation of the dicationic mixture (vide infra).

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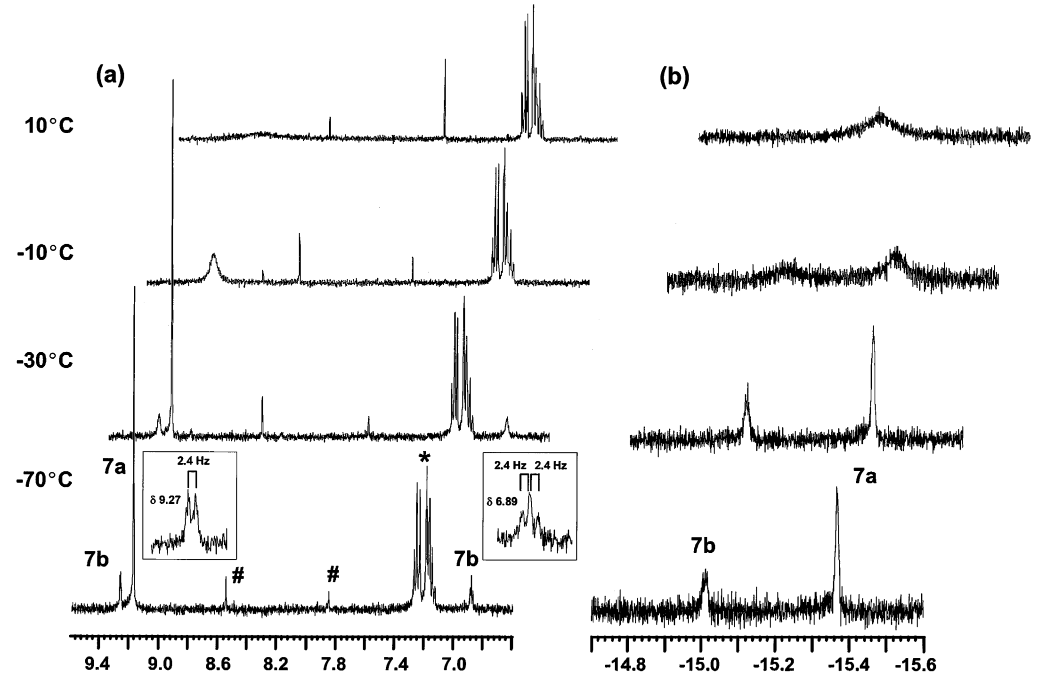
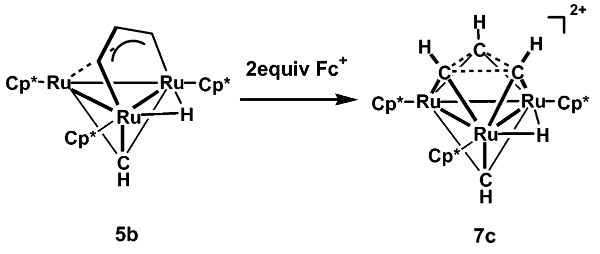


Figure 2. Variable-temperature ^{1}H NMR spectra of the dicationic complexes [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^3-CHCMeCH)(μ-H)]$^{2+}$ (**7a**,**b**) showing the regions for the methine protons (a) and the hydrides (b) in acetone-d_6. Signals marked with an asterisk (*) are derived from residual toluene in the sample. The signal found at δ 8.55 marked with a pound sign (#) is derived from a decomposed product due to moisture, and the methine signal of the μ_3-C$_3$ ring of **8** formed by deprotonation is also found at δ 7.86.

The two methine proton resonances of the μ_3-η^3-C$_3$ ring of **7a** were observed to be equivalent at δ 9.18 (2H) as a singlet. This suggests that complex **7a** has a plane of symmetry bisecting the μ_3-η^3-C$_3$ ring. Therefore, the hydrido ligand must be located on the Ru−Ru edge bridged by the μ-CMe group.

Because the proportion of **7b** in solution in the isomeric mixture was low at −70 °C, the ^{13}C signals derived from **7b** were not fully assigned, and the $J_{\mathrm{C-H}}$ data of the ring carbon characteristic of the μ_3-η^3-C$_3$ ring structure were missing. Complex **7b** was thus characterized mainly on the basis of the ^{1}H NMR spectra. Although spectroscopic evidence for the μ_3-η^3-C$_3$ ring of **7b** was not obtained, the fact that deprotonation of the mixture of **7a** and **7b** afforded only one isomer, **8**, containing a μ_3-η^3-C$_3$ ring (vide infra), strongly suggests that complex **7b** also contains a μ_3-η^3-C$_3$ ring, just as **7a** does. And, the ^{1}H NMR data indicated that **7b** was regioisomeric with **7a** with respect to the position of the hydrido ligand. The hydride of **7b** was most likely coordinated to the Ru−Ru edge bridged by the μ-CH group. The two methine protons of the C$_3$ ring are, therefore, placed in nonequivalent environments. In the ^{1}H NMR spectra, one of them was observed at δ 9.27 as a doublet ($J_{\mathrm{H-H}}$ = 2.4 Hz) and the other was observed at δ 6.89 as a pseudotriplet due to additional coupling with the hydrido ligand ($J_{\mathrm{H-H}}$ = 2.4 and 2.4 Hz).

In order to confirm the equilibrium between **7a** and **7b**, we prepared an unsubstituted μ_3-η^3-C$_3$ complex, [(Cp*Ru)$_3$(μ_3-η^3-C$_3$H$_3$)(μ_3-CH)(μ-H)]$^{2+}$ (**7c**), through the two-electron oxidation of the unsubstituted diruthenaallyl complex (Cp*Ru)$_3$(μ_3-η^1:η^3:η^1-CHCHCH)(μ_3-CH)(μ-H) (**5b**)^{14} (eq 7). Treatment of **5b** with 2 molar equiv of Fc$^+$ brought about a rapid color change and resulted in the quantitative formation of a red precipitate of **7c**. Exclusive formation of **7c** was confirmed by means of ^{1}H and ^{13}C NMR spectroscopy.



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Signals for the hydride of **7a** and **7b** were observed at δ −15.37 and −15.00 in the ^{1}H NMR spectra measured at −70 °C, respectively (Figure 2b). As mentioned above, the intensity ratio of the signals was 67:33 at −70 °C. They broadened with an increase in the temperature. They coalesced into a broad signal at 10 °C. Signals for both the μ_3-methylidyne proton and the methyl proton on the μ_3-η^3-C$_3$ ring of **7a**,**b** also coalesced at ambient temperature.

Because of the efficiently rapid interconversion between **7a** and **7b** stemming from the dynamic behavior of the hydrido ligand, two signals of the Cp* groups were observed at δ 2.06 and 2.08 in an intensity ratio of 2:1. These two signals of the Cp* groups never broadened and coalesced, in spite of the rise in temperature. This clearly shows that the μ_3-η^3-C$_3$ ring is rigid and rotation of the μ_3-η^3-C$_3$ ring was negligible, at least within the NMR time scale. The μ_3-η^3-C$_3$ ring of the monocationic complex [{Cp*Ru(μ-H)}$_3$(μ_3-η^3-C$_3$HRMe)]$^+$ (**4**) has been also revealed to be rigid.^{8}

Deprotonation of the Dicationic Mixture 7a,b. The dicationic mixture **7a**,**b** undergoes deprotonation on dissolution in acetone containing adventitious water. Deprotonation was accelerated by the addition of MeOH to the acetone solution of **7** due to an increase in polarity of the solvent (see the Supporting Information). Deprotonation of the dicationic mixture quantitatively proceeded by the addition of a base, such as amine. Treatment of **7a**,**b** with an excess amount of triethylamine in

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(14) Complex **5b** was obtained by the thermolysis of the μ_3-η^2-vinylidene μ_3-η^2(||)-ethyne complex (Cp*Ru)$_3$(μ_3-η^2(||)-HCCH)(μ_3-η^2-C=CH$_2$)(μ-H).^{13c} Details of the formation of **5b**, including C−C bond cleavage and formation across the Ru$_3$ plane, will be published elsewhere.

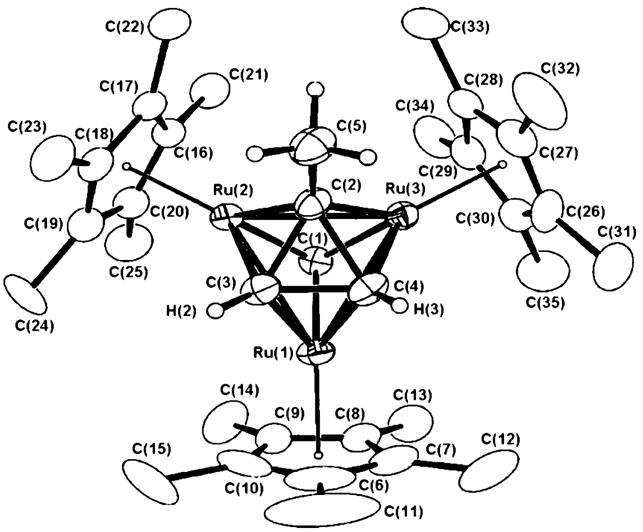
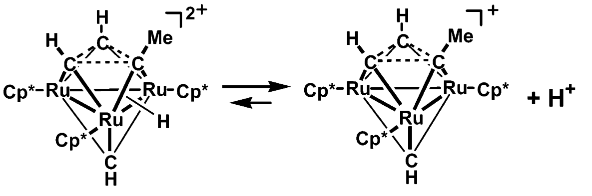


Figure 3. Molecular structure and labeling scheme of **8** with thermal ellipsoids at the 40% probability level. The anionic moiety (BPh_4^-) is omitted for clarity.

CH_2Cl_2 resulted in quantitative formation of a hexafluorophosphate salt of the monocationic complex $[(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)]^+$ (**8**), containing a μ_3-η^3-C_3 ring (eq 8). Complex **8** was fully characterized on the basis of the ^1H and ^{13}C NMR and IR spectra as well as analytical data.



(8)

7a and 7b **8**

Protonation of **8** by CF_3SO_3H afforded the dicationic mixture **7a**,**b**. A signal assignable to the hydride of the dicationic mixture appeared at δ −15.48. However, no reaction occurred with CF_3COOH. In the ^1H NMR spectra of **8**, a signal of the methine proton of the μ_3-η^3-C_3 ring was observed at δ 7.77. The resonances for the ring carbons were observed at δ 109.9 (s, −*C*Me) and 158.2 (d, $J_{C-H} = 189.1$ Hz, −*C*H). These shifts are slightly higher than those for the dicationic complexes **7a**,**c**.

The J_{C-H} value of 189.1 Hz was smaller than that observed in **7a** by 8 Hz. This is probably due to reduction of the s character of the hybrid orbital at the ring carbon in **8** in comparison with that of **7a** as a result of enhanced back-donation from the metal center to the C_3 ring.

A single crystal suitable for the X-ray diffraction studies was obtained by changing the counteranion from PF_6^- to BPh_4^-. The structure of **8** is shown in Figure 3, and relevant bond lengths and angles are given in Table 1. The crystal data for **8-BPh₄** are given in the Experimental Section (Table 4).

The C_3 plane is approximately parallel to the Ru_3 triangle in staggered form, which is very similar to the case for the reported tris(μ-carbene) complexes $[\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^3\text{-}C_3HMe_2)]^+$ (**4b**)[8] and $(Cp^*Ru)_3(\mu_3\text{-}CO)(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)$.[12] The average Ru−Ru distance (2.70 Å) corresponds to an Ru−Ru single bond and is slightly shorter than those of **4b** (average 2.81 Å). The difference in the Ru−Ru bond lengths between **8** and **4b** likely arises from the μ_3-methylidyne ligand placed on the opposite face of the Ru_3 plane. The μ_3-methylidyne ligand seems to bind the ruthenium atoms more tightly than does the μ-hydrido ligand. The Ru−Ru length is rather close to that of the neutral complex $(Cp^*Ru)_3(\mu_3\text{-}CO)(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)$ (average 2.74 Å),[12] which contains a μ_3-carbonyl ligand.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 8

Ru(1)−Ru(2)	2.7018(4)	Ru(2)−C(2)	2.075(2)
Ru(1)−C(3)	2.067(2)	Ru(3)−C(2)	2.077(2)
Ru(2)−C(1)	2.005(2)	C(2)−C(5)	1.496(3)
Ru(3)−C(1)	2.010(2)	Ru(1)−C(1)	2.014(2)
C(2)−C(3)	1.605(3)	Ru(2)−Ru(3)	2.6996(5)
C(3)−C(4)	1.582(3)	Ru(2)−C(3)	2.057(2)
Ru(1)−Ru(3)	2.6870(4)	Ru(3)−C(4)	2.049(2)
Ru(1)−C(4)	2.055(2)	C(2)−C(4)	1.610(3)
Ru(2)−Ru(1)−Ru(3)	60.126(11)	Ru(2)−C(2)−C(3)	66.56(11)
C(3)−Ru(1)−C(4)	45.12(9)	C(3)−C(2)−C(5)	120.8(2)
Ru(3)−Ru(2)−C(2)	49.46(6)	Ru(1)−C(3)−C(4)	67.04(12)
Ru(1)−Ru(3)−C(4)	49.20(6)	Ru(1)−C(4)−Ru(3)	81.79(8)
Ru(1)−C(1)−Ru(2)	84.48(8)	C(2)−C(4)−C(3)	60.35(14)
Ru(2)−C(2)−Ru(3)	81.11(8)	Ru(3)−Ru(1)−C(4)	49.00(6)
C(3)−C(2)−C(4)	58.93(14)	Ru(1)−Ru(2)−C(3)	49.23(6)
Ru(1)−C(3)−Ru(2)	81.85(8)	Ru(1)−Ru(3)−Ru(2)	60.209(11)
C(2)−C(3)−C(4)	60.71(14)	C(2)−Ru(3)−C(4)	45.95(9)
Ru(3)−C(4)−C(2)	67.93(12)	Ru(2)−C(1)−Ru(3)	84.52(8)
Ru(2)−Ru(1)−C(3)	48.92(6)	Ru(2)−C(2)−C(5)	131.06(17)
Ru(1)−Ru(2)−Ru(3)	59.665(10)	C(4)−C(2)−C(5)	121.45(19)
C(2)−Ru(2)−C(3)	45.69(9)	Ru(2)−C(3)−C(2)	67.75(11)
Ru(2)−Ru(3)−C(2)	49.43(6)	Ru(1)−C(4)−C(3)	67.84(12)
Ru(1)−C(1)−Ru(3)	83.78(8)		

The C_3 ring forms a nearly equilateral triangle with edges of 1.605(3), 1.610(3), and 1.582(3) Å. Notably, these C−C bond lengths of the C_3 ring are significantly longer than that for the normal C−C single bond ($C(sp^3)-C(sp^3) = 1.537 \pm 0.005$ Å).[15] In contrast, the C−C bond lengths of mononuclear η^3-C_3R_3 complexes mostly lie in the range from 1.40 to 1.45 Å.[16] Such an elongation of the C−C bond is the most striking feature of the trinuclear μ_3-η^3-C_3 complex. The average C−C bond lengths of other trinuclear μ_3-η^3-C_3 complexes are also significantly large (**4b**, 1.56 Å;[8] $(Cp^*Ru)_3(\mu_3\text{-}CO)(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)$, 1.58 Å[12]). In addition, the bend-back angles of the substituents from the C_3 plane are significantly larger than those for the mononuclear η^3-cyclopropenyl complexes; C(5), H(2), and H(3) are bent away by 53.6, 55.7, and 55.4° from the C_3 plane, respectively. Those of the mononuclear η^3-cyclopropenyl complexes lie in the range from 13.7 to 43.5°.[16]

Long C−C bond lengths and large bend-back angles indicate that the C_3 ring is coordinated to the Ru_3 core in a manner different from those found in the mononuclear η^3-cyclopropenyl complexes. These structural features found in **8** strongly suggest the carbenic character of the ring carbon and are quite consistent with the large J_{C-H} values, 177−209 Hz (vide supra).

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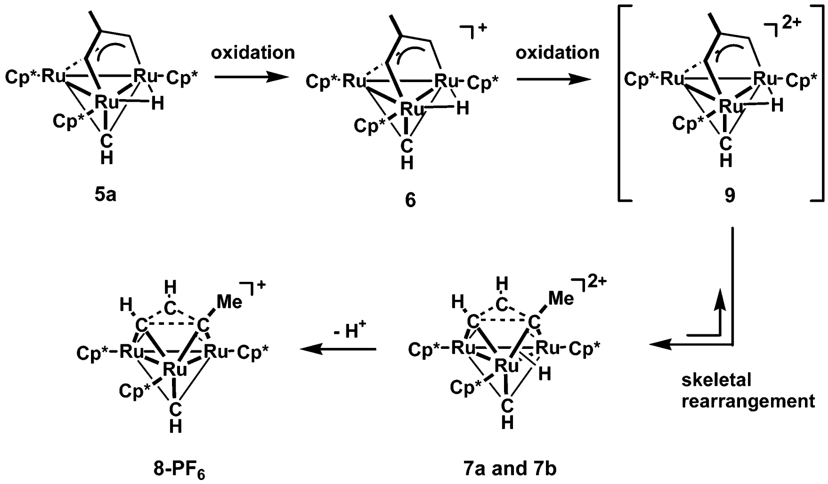
(15) *Spec. Publ. Chem. Soc.* **1965**, *No. 18*, S14s−S15s.

(16) For example: (a) Weaver, D. L.; Tuggle, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 6506−6507. (b) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1971**, *10*, 1504−1510. (c) McClure, M. D.; Weaver, D. L. *J. Organomet. Chem.* **1973**, *54*, C59−C61. (d) Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Inorg. Chem.* **1979**, *18*, 1687−1691. (e) Gompper, R.; Bartmann, E.; Nöth, H. *Chem. Ber.* **1979**, *112*, 218−233. (f) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310−1316. (g) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574−1583. (h) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1754−1761. (i) Churchill, M. R.; Fettinger, J. C. *J. Organomet. Chem.* **1985**, *290*, 375−386. (j) Hughes, R. P.; Lambert, J. M.; Whitman, D. W.; Hubbard, J. L.; Henry, W. P.; Rheingold, A. L. *Organometallics* **1986**, *5*, 789−797. (k) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 833−834. (l) Schrock, R. R.; Murdzek, J. S.; Freudenberger, J. H.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1986**, *5*, 25−33. (m) Hughes, R. P.; Tucker, D. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3069−3074. (n) Blunden, R. B.; Cloke, F. G. N.; Hitchcock, P. B.; Scott, P. *Organometallics* **1994**, *13*, 2917−2919. (o) Ghilardi, C. A.; Innocenti, P.; Midollini, S.; Orlandini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1109−1113.

Scheme 2

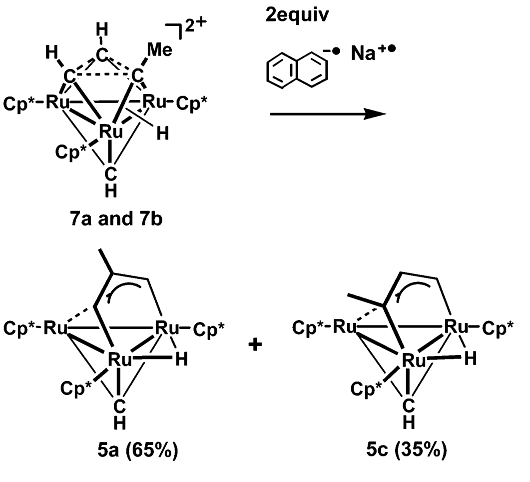


Oxidation of **5a** generating the monocationic μ_3-η^3-C_3 complex **8** proceeds by way of two initial steps of one-electron oxidation, leading to the dicationic μ_3-diruthenaallyl complexes **9** via the monocationic complex **6**, skeletal rearrangement involving C−C bond formation on the dicationic metal centers of **9**, and subsequent deprotonation from the dicationic hydrido complex **7**, as shown in Scheme 2.

Unfortunately, signals assignable to **9** were not detected when the reaction was monitored by means of ^{1}H NMR spectroscopy. This is likely due to rapid conversion of **9** to **7a**,**b** via a skeletal rearrangement of the diruthenaallyl moiety. A C_3-ring ligand was formed via bond formation between the terminal carbon atoms of the allylic moiety of the dicationic intermediate **9**.

Direct bond formation across the two metal centers has been well investigated in A-frame-type complexes.[17] There is still argument regarding the mechanism, but some of the reactions were considered to proceed via a 1,2-shift of the alkyl group followed by the usual reductive elimination at a metal center. At present, we do not have any positive evidence to show how the C_3 ring in **7** was formed.

Reduction of the Dicationic Mixture 7a,b. Treatment of the dicationic mixture **7a**,**b**, with 2 equiv of sodium naphthalenide at 25 °C resulted in formation of a mixture of two stereoisomeric neutral diruthenaallyl complexes, **5a**,**c**, in the ratio 65:35 (eq 9). The diruthenaallyl complexes **5a**,**c** were formed



(9)

as the result of C(H)−C(H) and C(Me)−C(H) bond cleavage of the μ_3-η^3-C_3 ring, respectively. Further reduction leading to the formation of an anionic complex was not observed during this reaction. This reduction is quite different from the reduction of carbonyl dimetallaallyl clusters, which yields an anionic species followed by degradation.[11a] Since **5a**,**c** could not be separated from each other by column chromatography, they were characterized as a mixture by means of ^{1}H and ^{13}C NMR spectroscopy. Complex **5a** was unambiguously identified by comparing the spectra with those of the authentic sample.[10]

In the ^{1}H NMR spectra of the mixture, three Cp* signals arising from **5c** were observed at δ 1.52, δ 1.83, and δ 1.88, while those of **5a** were observed as a set of two signals with an intensity ratio of 2:1 (δ 1.58 and 1.90). The resonance of the methine protons of **5a** was observed at δ 8.24 as a singlet, and those of **5c** appeared at δ 5.43 (dd, J_{H-H} = 5.6, 4.0 Hz) and δ 8.48 (d, J_{H-H} = 5.6 Hz) with mutual coupling. Long-range coupling between the hydride and the allylic proton located at the 2-position has been often observed for the μ_3-dimetallaallyl complexes, and the value of 4.0 Hz for **5c** lies in the reported range (0.5−5.0 Hz).[13,15,18] The ^{1}H NMR spectrum of **5c** was quite similar to that of the μ_3-ethylidyne μ_3-η^1:η^3:η^1-1-methyldiruthenaallyl complex **5d** (Chart 1), which was synthesized by the reaction of $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**) with three molecules of acetylene.[13c] The ^{13}C NMR spectrum was also consistent with this structure.

Complexes **5a**,**c** were thermally stable and did not decompose, even at 160 °C. In addition, the ratio between **5a** and **5c** did not change upon heating at 160 °C for 24 h. This shows that isomerization between **5a** and **5c** did not take place, at least at 160 °C. Thus, the ratio of **5a** to **5c** seems to be kinetically

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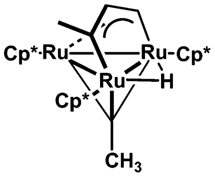
[17] For example: (a) Stockland, R. A., Jr.; Janka, M.; Hoel, G. R.; Rath, N. P.; Anderson, G. K. *Organometallics* **2001**, *20*, 5212−5219. (b) Kramarz, K. W.; Eisenberg, R. *Organometallics* **1992**, *11*, 1997−1999. (c) Azam, K.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1396−1399.

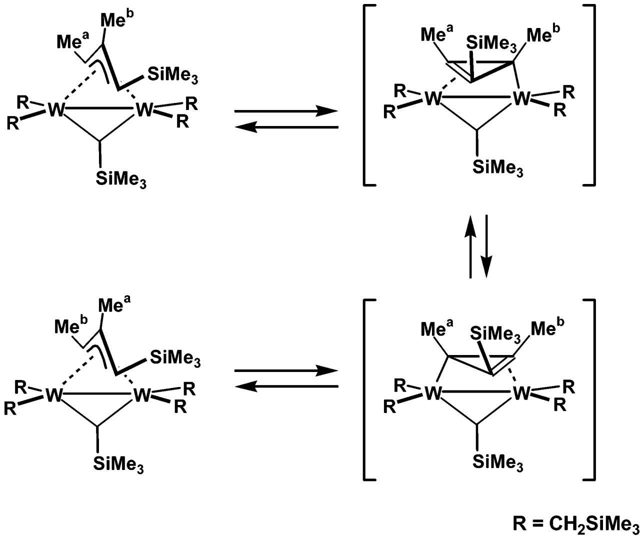
[18] (a) Bruce, M. I.; Cairns, M. A.; Cox, A.; Green, M.; Smith, M. D. H.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1970**, 735. (b) Cox, A.; Woodward, P. *J. Chem. Soc. A* **1971**, 3559−3603. (c) Evans, M.; Hursthouse, M.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Chem. Commun.* **1972**, 545−546. (d) Gambino, O.; Valle, M.; Aime, S.; Vaglio, G. A. *Inorg. Chim. Acta.* **1974**, *8*, 71−75. (e) Castiglioni, M.; Milone, L.; Osella, D.; Vaglio, G. A.; Valle, M. *Inorg. Chem.* **1976**, *2*, 394−396. (f) Jangala, C.; Rosenberg, E.; Skinner, D.; Aime, S.; Milone, L.; Sappa, E. *Inorg. Chem.* **1980**, *19*, 1571−1575. (g) Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Rosenberg, E. *Organometallics* **1982**, *1*, 640−644. (h) Churchill, M. R.; Lake, C. H.; Lashewycz-Rubycz, R. A.; Yao, H.; McCargar, R. D.; Keister, J. B. *J. Organomet. Chem.* **1993**, *452*, 151−160. (i) Yao, H.; McCargar, R. D.; Allendoerfer, R. D.; Keister, J. B. *Organometallics* **1993**, *12*, 4283−4285. (j) Kallinen, K. O.; Ahlgrén, M.; Pakkanen, T. T.; Pakkanen, T. A. *J. Organomet. Chem.* **1996**, *510*, 37−43. (k) Bruce, M. I.; Fun, H.-K.; Nicholson, B. K.; Shawkataly, O.; Thomson, R. A. *J. Chem. Soc., Dalton Trans.* **1998**, 751−754. (l) Ellis, D.; Farrugia, L. J. *J. Cluster Sci.* **2001**, *12*, 243−257. (m) Xia, C.-G.; Bott, S. G.; Richmond, M. G. *J. Chem. Crystallogr.* **2003**, *33*, 681−687.

Chart 1



5d

Scheme 3

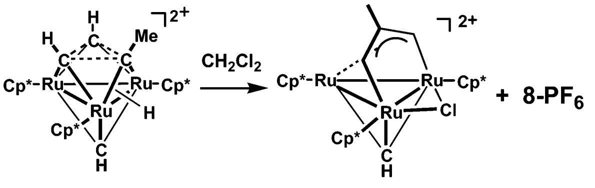


controlled in the reduction step, and the ratio represents the strength of the C−C bond of the μ_3-C_3 ring; i.e., the C(H)−C(H) bond was more readily cleaved than the C(Me)−C(H) bond by ca. 4 times.

Chisholm et al. reported that two CMe groups in the μ-allyl group of $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}CMeCMeCSiMe_3)$ mutually exchange positions within the NMR time scale by way of a μ-C_3 ring intermediate (Scheme 3).[19a] Similar skeletal rearrangement involving formation of a μ_3-C_3 ring intermediate was also proposed for the formation of a trimetallic dimetallaallyl complex by Stone and co-workers.[19b] Thus, the formation of **5c** by the reduction of **7a**,**b**, which was formed by the oxidation of **5a**, could be a good model for the some unusual skeletal rearrangements performed on a multimetallic center.

Formation of a Dicationic μ_3-η^1:η^3:η^1-2-Methyldiruthenaallyl Complex. As mentioned above, we proposed the dicationic μ_3-diruthenaallyl complex **9** as an intermediate of the two-electron oxidation of **5a**. Although no direct evidence of the formation of **9** was obtained, we fortunately isolated a hexafluorophosphate salt of dicationic complex **10** in the reaction of **7** with chloroform. The dicationic complex **10** has a μ_3-diruthenaallyl moiety analogous to that of the dicationic intermediate **9**.

Treatment of the mixture **7a**,**b** with the chlorinated solvents CH_2Cl_2, $CHCl_3$, and CCl_4 resulted in substitution of the hydrido ligand with chloride and afforded the dicationic μ_3-methylidyne μ-chloro μ_3-η^1:η^3:η^1-2-methyldiruthenaallyl complex $[(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CHCMeCH)(\mu\text{-}Cl)]^{2+}$ (**10**) (eq 10). While the reaction of the dicationic mixture **7** with CH_2Cl_2 required heating in a sealed bottle at 100 °C, the reaction with $CHCl_3$ proceeded smoothly at room temperature. Although the reaction of **7** with CCl_4 took place rapidly, several unidentified products were obtained in addition to **10**. During these reactions, a considerable amount of the monocationic complex **8** was formed as a result of deprotonation. Complex **10** was isolated by recrystallization from the cold CH_2Cl_2 solution of the mixture and fully characterized by means of ^1H and ^{13}C NMR and IR spectra as well as elemental analysis.



(10)

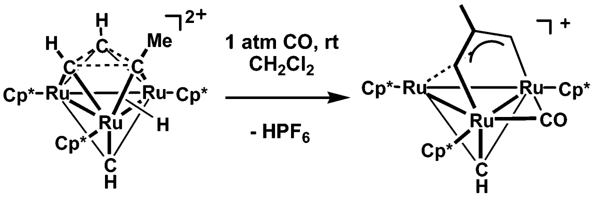
7a and 7b **10 (76 %)** **(24 %)**

A characteristic feature of the NMR data of **10** is the significant downfield shift of the signals of the allylic moiety. In the ^1H NMR spectra, the methine signal of the μ_3-diruthenaallyl ligand of **10** was observed at δ 10.09 as a singlet. This value is lower by about 2 ppm than that of the neutral diruthenaallyl complex **5a** (δ 8.24). The ^{13}C signals of the methine carbons of the μ_3-diruthenaallyl moiety of **10** and **5a** are δ 195.4 (d, $J_{C-H} = 166.7$ Hz) and 174.6 (d, $J_{C-H} = 141.9$ Hz), respectively. The increase in the J_{C-H} value implies weakening of the back-donation from the metal center to the allylic moiety in **10,** owing to the reduction in electron density in **10**.

X-ray diffraction studies were performed by the use of a dark green single crystal obtained from cold CH_2Cl_2 solution at −30 °C. The structure of **10** is represented in Figure 4, and selected bond lengths and angles are given in Table 2. To the best of our knowledge, this is the first structurally elucidated example of a cationic μ_3-diruthenaallyl complex. Figure 4 clearly shows the μ_3-diruthenaallyl structure of **10**.

Although the NMR studies indicate weak back-donation from the cationic metal centers to the allylic moiety, the C−C bond lengths (C(2)−C(3), 1.425(3) Å; C(3)−C(4), 1.430(3) Å) are not so different from that of the neutral **5a** (1.41 Å). These values lie in the range reported for the μ_3-diruthenaallyl complexes.[7,10,13c,19a−d,h,j−l,20]

Reaction of the Dicationic Mixture with Carbon Monoxide. The presence of the μ_3-diruthenaallyl isomer **9** in the equilibrium was also implied by the reaction of the mixture of dicationic complexes **7a**,**b** with carbon monoxide. Treatment of the mixture with 1 atm of CO in CH_2Cl_2 solution at room temperature resulted in quantitative formation of the hexafluorophosphate salt of the monocationic μ_3-methylidyne μ-carbonyl μ_3-η^1:η^3:η^1-2-methyldiruthenaallyl complex $[(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CHCMeCH)(\mu\text{-}CO)]^+$ (**11**) (eq 11). The μ_3-diruthenaallyl complex **11** was characterized by means of ^1H and ^{13}C NMR and IR spectroscopy. A red single crystal of the tetraphenylborate salt of **11** suitable for the diffraction studies was obtained by changing the counteranion to BPh_4^-, and the diruthenaallyl structure can be confirmed by the X-ray diffraction studies. There were two independent molecules in the unit



(11)

7a and 7b **11-PF$_6$ (96 %)**

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(19) (a) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 1151−1153. (b) Jeffery, J. C.; Mead, K. A.; Razay, H.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 867−868.

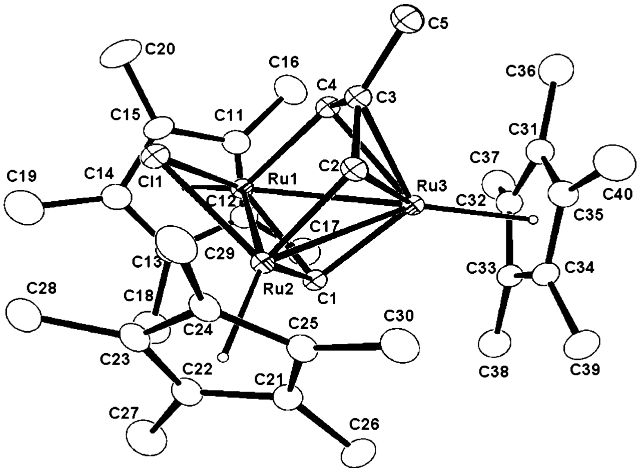

Figure 4. Molecular structure and labeling scheme of **10** with thermal ellipsoids at the 40% probability level. The anionic moiety (PF_6^-) and solvent molecules (CH_2Cl_2) are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 10

Ru(1)−Ru(2)	2.6775(3)	Ru(2)−C(2)	2.030(2)
Ru(1)−C(4)	2.031(2)	Ru(3)−C(2)	2.123(2)
Ru(2)−C(1)	2.020(2)	C(2)−C(3)	1.425(3)
Ru(3)−C(1)	2.006(5)	Ru(1)−C(1)	2.014(2)
Ru(3)−C(4)	2.131(2)	Ru(2)−Ru3)	2.7341(3)
C(3)−C(5)	1.508(3)	Ru(2)−Cl(1)	2.3458(6)
Ru(1)−Ru(3)	2.7357(3)	Ru(3)−C(3)	2.244(2)
Ru(1)−Cl(1)	2.3446(6)	C(3)−C(4)	1.430(3)
Ru(2)−Ru(1)−Ru(3)	60.663(7)	Ru(1)−Ru(3)−C(2)	83.25(7)
Ru(2)−Ru(1)−C(4)	86.41(7)	Ru(2)−Ru(3)−C(2)	47.37(6)
Ru(3)−Ru(1)−C(4)	50.50(7)	C(1)−Ru(3)−C(4)	94.18(9)
C(1)−Ru(1)−C(4)	97.07(10)	Ru(2)−C(2)−C(3)	122.99(18)
Ru(1)−Ru(2)−C(1)	48.32(7)	C(2)−C(3)−C(5)	121.2(2)
Ru(3)−Ru(2)−C(1)	47.02(7)	Ru(1)−C(4)−C(3)	122.99(17)
Cl(1)−Ru(2)−C(2)	83.19(7)	Ru(2)−Ru(1)−C(1)	48.50(7)
Ru(1)−Ru(3)−C(1)	47.24(7)	Ru(3)−Ru(1)−C(1)	47.00(7)
Ru(2)−Ru(3)−C(1)	47.43(7)	Cl(1)−Ru(1)−C(4)	82.93(7)
C(1)−Ru(3)−C(2)	94.39(9)	Ru(1)−Ru(2)−Cl(1)	55.171(15)
Ru(2)−C(2)−Ru(3)	82.31(9)	Ru(3)−Ru(2)−Cl(1)	100.297(16)
C(2)−C(3)−C(4)	116.4(2)	Cl(1)−Ru(2)−C(1)	103.25(7)
Ru(1)−C(4)−Ru(3)	82.16(8)	Ru(1)−Ru(3)−Ru(2)	58.616(7)
Ru(2)−Ru(1)−Cl(1)	55.212(16)	Ru(1)−Ru(3)−C(4)	47.34(7)
Ru(3)−Ru(1)−Cl(1)	100.283(17)	Ru(2)−Ru(3)−C(4)	83.09(6)
Cl(1)−Ru(1)−C(1)	103.47(7)	C(2)−Ru(3)−C(4)	69.56(9)
Ru(1)−Ru(2)−Ru(3)	60.721(7)	Ru(3)−C(2)−C(3)	75.61(14)
Ru(1)−Ru(2)−C(2)	86.50(7)	C(4)−C(3)−C(5)	121.8(2)
Ru(3)−Ru(2)−C(2)	50.31(7)	Ru(3)−C(4)−C(3)	75.26(14)
C(1)−Ru(2)−C(2)	96.90(9)		

cell, and one of them contains a disordered structure in the diruthenaallyl moiety and the μ-carbonyl group. Figure 5 represents the structure of the nondisordered molecule of **11**, and relevant bond lengths and angles are given in Table 3.

Figure 5 clearly shows the μ_3-diruthenaallyl structure of **11**. The C−C bond lengths of the allylic moiety are almost the same as those of **5a** and **10**, in spite of the difference in charge of the trimetallic core (C(2)−C(3), 1.427(4) Å; C(3)−Ru(4), 1.419(4) Å).

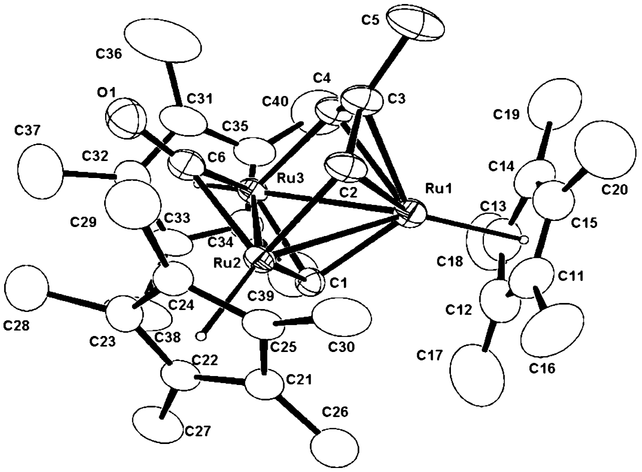

Figure 5. Molecular structure and labeling scheme of the cationic moiety of **11-BPh$_4$** with thermal ellipsoids at the 40% probability level. The anionic moiety is omitted for clarity. One of the two independent molecules in the unit cell is shown.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 11

Ru(1)−Ru(2)	2.7116(3)	Ru(3)−C(1)	1.994(3)
Ru(1)−C(2)	2.153(3)	C(2)−C(3)	1.427(4)
Ru(2)−Ru(3)	2.7060(3)	C(6)−O(1)	1.175(4)
Ru(2)−C(6)	2.023(3)	Ru(1)−C(1)	2.032(3)
Ru(3)−C(6)	2.045(3)	Ru(1)−C(4)	2.164(3)
C(3)−C(5)	1.516(4)	Ru(2)−C(2)	2.015(3)
Ru(1)−Ru(3)	2.7247(3)	Ru(3)−C(4)	2.018(3)
Ru(1)−C(3)	2.235(3)	C(3)−C(4)	1.419(4)
Ru(2)−C(1)	1.993(3)		
Ru(2)−Ru(1)−Ru(3)	59.705(9)	Ru(1)−Ru(3)−C(4)	51.70(9)
Ru(2)−Ru(1)−C(4)	82.72(8)	Ru(2)−Ru(3)−C(4)	85.54(9)
Ru(3)−Ru(1)−C(4)	47.06(8)	C(1)−Ru(3)−C(6)	94.95(13)
C(2)−Ru(1)−C(4)	68.17(12)	Ru(1)−C(2)−C(3)	74.15(19)
Ru(1)−Ru(2)−C(2)	51.67(9)	C(2)−C(3)−C(5)	121.8(3)
Ru(3)−Ru(2)−C(2)	86.31(9)	Ru(1)−C(4)−C(3)	73.92(19)
C(1)−Ru(2)−C(6)	95.69(12)	Ru(2)−C(6)−O(1)	139.0(3)
Ru(1)−Ru(3)−C(1)	47.99(9)	Ru(2)−Ru(1)−C(2)	47.25(8)
Ru(2)−Ru(3)−C(1)	47.23(9)	Ru(3)−Ru(1)−C(2)	83.26(9)
C(1)−Ru(3)−C(4)	98.93(13)	C(1)−Ru(1)−C(4)	93.18(12)
Ru(1)−C(2)−Ru(2)	81.08(11)	Ru(1)−Ru(2)−C(1)	48.26(9)
C(2)−C(3)−C(4)	116.4(3)	Ru(3)−Ru(2)−C(1)	47.26(9)
Ru(1)−C(4)−Ru(3)	81.24(11)	C(1)−Ru(2)−C(2)	99.20(13)
Ru(2)−C(6)−Ru(3)	83.38(12)	Ru(1)−Ru(3)−Ru(2)	59.905(9)
Ru(2)−Ru(1)−C(1)	47.03(9)	Ru(1)−Ru(3)−C(6)	93.53(9)
Ru(3)−Ru(1)−C(1)	46.81(9)	Ru(2)−Ru(3)−C(6)	47.96(9)
C(1)−Ru(1)−C(2)	93.62(12)	C(4)−Ru(3)−C(6)	79.98(13)
Ru(1)−Ru(2)−Ru(3)	60.389(9)	Ru(2)−C(2)−C(3)	124.3(2)
Ru(1)−Ru(2)−C(6)	94.44(9)	C(4)−C(3)−C(5)	121.6(3)
Ru(3)−Ru(2)−C(6)	48.66(9)	Ru(3)−C(4)−C(3)	125.3(2)
C(2)−Ru(2)−C(6)	80.74(13)	Ru(3)−C(6)−O(1)	137.5(3)

In both ^{1}H and ^{13}C NMR spectra, signals stemming from the diruthenaallyl moiety of **11** appeared between those of neutral **5** and dicationic **10**. The methine proton of the diruthenaallyl moiety of **11** was observed at δ 8.55 as a singlet, while those of **5a** and **10** appeared at δ 8.24 and 10.09, respectively. The ^{13}C signal of the α-carbon was observed at δ 182.4 as a doublet (J_{C-H} = 146.5 Hz), which also appeared between those of **5a** (δ 174.6) and **10** (δ 195.4). The J_{C-H} value was also an intermediate value.

Thus, the chemical shift and the J_{C-H} value of the diruthenaallyl moiety have a close relationship with the number of positive charges on the Ru$_3$ core; as the positive charge increases, the methine signal shifts significantly downfield and

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(20) (a) Parkins, A. W.; Fischer, E. O.; Huttner, G.; Regler, D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 633. (b) Aime, S.; Osella, D.; Deeming, A. J.; Arce, A. J.; Hursthouse, M. B.; Dawes, H. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1459−1463. (c) Ziller, J. W.; Bower, D. K.; Dalton, D. M.; Keister, J. B.; Churchill, M. R. *Organometallics* **1989**, *8*, 492−497. (d) Churchill, M. B.; Buttrey, L. A.; Keister, J. B.; Ziller, J. W.; Janik, T. S.; Striejewske, W. S. *Organometallics* **1990**, *9*, 766−773. (e) Adams, K. J.; Barker, J. J.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 975−988. (f) Blake, A. J.; Dyson, P. J.; Gaede, P. E.; Johnson, B. F. G.; Parsons, S. *Organometallics* **1996**, *15*, 4100−4103. (g) Bruce, M. I.; Humphrey, P. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1997**, *545−546*, 207−218. (h) Hsu, M.-A.; Yeh, W.-Y.; Lee, G.-H.; Peng, S.-M. *J. Organomet. Chem.* **1999**, *588*, 32−41. (i) Xia, C.-G.; Bott, S. G.; Richmond, M. G. *J. Chem. Crystallogr.* **2003**, *33*, 681−687.

the J_{C-H} value increases. This trend is also observed in the μ_3-η^3-C_3 complexes and reflects weakening of the shielding effect and reduced back-donation from the three Ru atoms to the C_3 moiety in the dicationic species.

Since complex **11** is monocationic, deprotonation should take place during the reaction. It is noteworthy that the monocationic μ_3-η^3-C_3 complex **8** did not react with carbon monoxide, even under more forcing conditions. Thus, the reaction took place at the dicationic metal centers, and deprotonation is induced by the coordination of carbon monoxide.

Conclusion

Lowering of the HOMO level by introduction of a μ_3-methylidyne ligand into the cluster core was confirmed by the cyclic voltammograms of **5a** and **3a**, and introduction of the μ_3-methylidyne group enables us to isolate the paramagnetic 47e intermediate **6** as well as the dicationic mixture **7a**,**b**. The cyclic voltammograms shown in Figure 1 indicate that the first oxidation did not involve skeletal rearrangement and that the second oxidation step involves skeletal rearrangement from the μ_3-diruthenaallyl to the μ_3-η^3-C_3 ring structure. The extremely large J_{C-H} value of 196.6 Hz observed in **7a** strongly indicates that complex **7a** adopts a μ_3-η^3-C_3 ring structure. The C_3 ring structure was confirmed in the deprotonated complex **8** by means of X-ray diffraction studies. Thus, the oxidation of **5a**, affording the monocationic μ_3-η^3-C_3 complex **8**, proceeded by way of an EEC mechanism: i.e., (i) two steps of 1e oxidation, (ii) C−C bond formation on the Ru_3 cluster, and (iii) deprotonation.

This is a quite rare example of C−C bond formation occurring at a highly oxidized Ru_3 center, while C−C bond cleavage upon oxidation was reported for $Cp_2Ru_2(\mu\text{-cyclo-}C_8H_8)$[4a,b] and $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu\text{-}\eta^2{:}\eta^2\text{-HCCH})(\mu_3\text{-CO})_2$.[4c,d] In these complexes, the C−C bond was re-formed by reduction. The μ_3-diruthenaallyl skeleton has been transformed to the μ_3-η^3-C_3 ring structure, probably due to compensation of the electronic perturbation derived from the two-electron oxidation.

The notable features of the μ_3-η^3-C_3 ring of **8** are its unusually long C−C bond distances and large J_{C-H} values. These are most likely due to the carbenic character of the bridging carbons. The DFT calculations showed that the C_3 ligand was a resonance hybrid between the tris(μ-carbene) and μ_3-cyclopropenyl structures.

Although only **7a**,**b** were spectroscopically detected in the dicationic mixture, contribution of the dicationic μ_3-diruthenaallyl complex **9** in the equilibrated mixture would be implied by the reaction of the dicationic mixture **7a**,**b** with CH_2Cl_2 and CO. The reaction of **7a**,**b** with CH_2Cl_2 or CO afforded the dicationic μ-chloro μ_3-diruthenaallyl complex **10** and the monocationic μ-carbonyl μ_3-diruthenaallyl complex **11**, respectively. Although the mechanism of C−C bond cleavage by the coordination of the lone pair of a chlorine atom or CO to the dicationic metal center is not negligible at present, isolation of the dicationic diruthenaallyl complex **10** suggests that skeletal rearrangement between the μ_3-η^3-C_3 ring and μ_3-dimetallaallyl structures on the dicationic triruthenium core would be equally facile. We are now continuing research on the reactivities of the dicationic triruthenium clusters, especially functionalization of the hydrocarbyl ligand on the dicationic cluster.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of argon. All compounds were handled using Schlenk techniques. Dehydrated toluene, tetrahydrofuran, and pentane were purchased from Kanto Chemicals and stored under an argon atmosphere. Diethyl ether was dried over sodium−benzophenone ketyl and stored under an argon atmosphere. Acetone-d_6 was dried over MS-4A and stored under an argon atmosphere. Complex **5a** was prepared according to a method previously reported in ref 10. IR spectra were recorded on a Nicolet AVATAR 360 ESP spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 Fourier transform spectrometer with tetramethylsilane as an internal standard. Elemental analyses were performed on a Perkin-Elmer 2400II instrument. ESI-MS spectra were recorded on a JEOL JMS-T100CS spectrometer. Cyclic voltammograms were performed using a HOKUTO DENKO HSV-100 voltammetric analyzer interfaced to a personal computer. The working electrode was platinum, and the counter electrode was a platinum wire. The reference electrode was a silver wire housed in a glass tube sealed with a porous Vycor tip and filled with a 0.1 M solution of $AgNO_3$ in acetonitrile. The data obtained relative to a reference electrode (Ag/Ag^+) were converted to the potential relative to the redox potential of ferrocene, which was measured under the same conditions at the same time. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$; Wako) was recrystallized from THF, dried under vacuum, and stored under an argon atmosphere. A concentration of ∼1 mM of complexes **5a** and **3a** in 0.1 M $TBAPF_6$ in THF was used.

X-ray Structure Determination. X-ray-quality crystals of **8-BPh$_4$**, **10-PF$_6$**, and **11-BPh$_4$** were obtained directly from the preparations described below and mounted on glass fibers. Diffraction experiments of **8-BPh$_4$**, **10-PF$_6$**, and **11-BPh$_4$** were performed on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) at −120, −100, and −150 °C, respectively. The structures were solved by the Patterson method and subsequent Fourier difference techniques. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2 using the SHELX-97 program package. Neutral atom scattering factors were obtained from the standard sources.[21] Crystal data and results of the analyses are given in Table 4.

Preparation of [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^1:η^3:η^1-CHCMeCH)(μ-H)]$^+$ (6). Toluene (10 mL) and (Cp*Ru)$_3$(μ_3-CH)(μ_3-CHCMeCH)(μ-H) (**5a**; 86.1 mg, 0.11 mmol) were charged in a 50 mL reaction flask. After $[Cp_2Fe](PF_6)$ (36.7 mg, 0.11 mmol) was added to the solution at room temperature, the solution was vigorously stirred for 2 h. The solution immediately turned from red to purple, and a purple precipitate was formed. The precipitate was separated by removing the supernatant including ferrocene and rinsed three times with 2 mL of toluene. The residual solid was then dried under reduced pressure, and 81.7 mg of a hexafluorophosphate salt of **6** was obtained as a purple solid (0.089 mmol, 80%). Methanol (10 mL) and the hexafluorophosphate salt of **6** (81.7 mg, 0.089 mmol) were charged in a 50 mL reaction flask. After an excess amount of $NaBPh_4$ (158.4 mg, 0.463 mmol) was added to the solution, the reaction flask was vigorously stirred at room temperature for 2 h. The precipitate was separated by decantation to remove the supernatant including $NaPF_6$ and remaining $NaBPh_4$. The residual solid was then dried under reduced pressure, and a 51.7 mg amount of a tetraphenylborate salt of **6** was obtained as a purple solid (53%). **6-PF$_6$**: ^{1}H NMR (400 MHz, 25 °C, acetone-d_6) δ 43.67 (brs, $w_{1/2} = 2100$ Hz). **6-BPh$_4$**: ^{1}H NMR (400 MHz, 25 °C, acetone-d_6): δ 6.78 (t, $J_{HH} = 7.2$ Hz, 4H, *p*-B*Ph*$_4$), 6.90 (dd, $J_{HH} = 7.2$, 7.2 Hz, 8H, *m*-B*Ph*$_4$), 7.31, (m, 8H, *o*-B*Ph*$_4$), 43.68 (br s, $w_{1/2} = 2120$ Hz, 45H, C_5Me_5). Anal. Calcd for $C_{59}H_{72}BRu_3$: C, 64.70; H, 6.63. Found: C, 64.24; H, 6.35. Due to its instability toward air, the complex **6-BPh$_4$** partially decomposed during carbon analysis. ESI mass spectra for **6-PF$_6$** and **6-BPh$_4$** could not be obtained, due to the fragmentation into bi- and monometallic compounds during ionization.

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

Table 4. Crystallographic Data for 8-BPh$_4$, 10-PF$_6$, and 11-BPh$_4$

	8-BPh$_4$	**10-PF$_6$**	**11-BPh$_4$**
(a) Crystal Data			
empirical formula	$C_{59}H_{71}BRu_3$	$C_{36}H_{53}Cl_3F_{12}P_2Ru_3$	$C_{60}H_{71}BORu_3$
formula wt	1094.18	1185.28	1122.19
cryst descripn	platelet	platelet	platelet
cryst color	red	green	red
cryst size (mm)	0.50 × 0.20 × 0.20	0.60 × 0.20 × 0.20	0.40 × 0.10 × 0.05
crystallizing soln	THF (−30 °C)	CH_2Cl_2 (−30 °C)	MeOH (−30 °C)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
lattice params			
a (Å)	19.918(4)	11.9434(2)	16.56750(10)
b (Å)	13.650(2)	16.1553(3)	17.3124(2)
c (Å)	20.532(4)	22.2949(3)	35.4645(3)
β (deg)	115.466(8)	96.7400(6)	95.5860(4)
V (Å^3)	5040.2(17)	4272.05(12)	10123.74(16)
Z	4	4	8
D_{calcd} (g cm^{-3})	1.442	1.843	1.473
measmt temp (°C)	−120	−100	−150
μ(Mo Kα) (mm^{-1})	0.925	1.389	0.924
(b) Intensity Measurements			
diffractometer	RAXIS-RAPID	RAXIS-RAPID	RAXIS-RAPID
radiation	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite
$2\theta_{max}$ (deg)	60	60	60
no. of rflns collected	47 921	50 503	89 389
no. of indep rflns	11 987 (R_{int} = 0.0327)	12 349 (R_{int} = 0.0199)	29 676 (R_{int} = 0.0328)
no. of obsd rflns (>2σ)	10 307	11 173	21 522
abs cor type	empirical	empirical	empirical
abs transmissn			
min	0.6610	0.4894	0.9085
max	1.0000	0.7685	1.0739
(c) Refinement (Shelxl-97)			
R1 ($I > 2\sigma(I)$)	0.0280	0.0347	0.0452
wR2 ($I > 2\sigma(I)$)	0.0702	0.0851	0.0884
R1 (all data)	0.0320	0.0393	0.0715
wR2 (all data)	0.0721	0.0877	0.0975
no. of data/restraints/params	11 502/0/597	12 349/0/534	28 750/0/1229
GOF	1.029	1.040	1.052
largest diff peak, hole (e Å^{-3})	0.865, −1.498	2.413, −1.459	2.102, −2.548

Reaction of 3a with an Equimolar Amount of [Cp$_2$Fe][PF$_6$]. Toluene (10 mL) and (Cp*Ru)$_3$(μ-H)$_4$(μ_3-η^1:η^3:η^1-CHCHCMe) (81.9 mg, 0.107 mmol) were charged in a reaction flask. After [Cp$_2$Fe][PF$_6$] (35.7 mg, 0.108 mmol) was added to the solution at 0 °C, the solution was vigorously stirred for 1 h. The solution turned from dark green to brown. Removal of the solvent under reduced pressure afforded 0.122 g of brown precipitate. The ^{1}H NMR spectrum of the mixture showed that all of **3a** was consumed and **4a** was formed in 33% yield as the main product. In addition to **4a**, formation of ferrocene and some other unidentified species was observed. Among the unidentified signals, a broad signal derived from a paramagnetic compound, which was considered to be a one-electron-oxidized product of **3a**, was observed at δ 4.51 ($w_{1/2}$ = 43.4 Hz), although this compound was not isolated and completely characterized. The yield of **4a** was estimated on the basis of the intensity of the Cp* signals of **4a**, using the produced ferrocene as an internal standard.

Reduction of Complex 6. THF (10 mL) and the hexafluorophosphate salt of **6** (47.2 mg, 0.0443 mmol) were charged in a reaction flask. After 1 equiv of (C$_5$Me$_5$)$_2$Co (15.3 mg, 0.0464 mmol) was added to the solution at room temperature, the solution was vigorously stirred for 2 h. The solution turned from purple to red. After the solvent was removed under reduced pressure, the residual solid was dissolved in 3 mL of toluene. The product was then purified by the use of column chromatography on neutral alumina (Merck Art. No. 1097) with toluene. A red band was collected, and a 28.2 mg amount of **5a** was obtained as a red solid by removal of the solvent in vacuo (0.0363 mmol, 82%). Formation of **5a** was confirmed by comparing its ^{1}H NMR spectrum with that of an authentic sample prepared by the method described in ref 10.

Preparation of [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^3-C$_3$H$_2$Me)(μ-H)]$^{2+}$ (7a,b). Toluene (10 mL) and (Cp*Ru)$_3$(μ_3-CH)(μ_3-CHCMeCH)(μ-H) (**5a**; 92.7 mg, 0.12 mmol) were charged in a 50 mL reaction flask. After [Cp$_2$Fe](PF$_6$) (74.0 mg, 0.24 mmol) was added to the solution at room temperature, the solution was vigorously stirred for 2 h. The solution turned from red to brown, and a brown precipitate was formed. The precipitate was then separated by removal of the supernatant including ferrocene. The brown solid was rinsed three times with 5 mL of toluene. The residual solid was dried under reduced pressure, and 0.116 g of the mixture of hexafluorophosphate salts of **7a**,**b** was obtained as a brown solid (0.11 mmol, 92%). Since **7a** and **7b** equilibrated with each other in solution, they were not separated from each other. The ratio between **7a**,**b** at −70 °C was estimated as 67:33 on the basis of the ^{1}H NMR spectrum of the mixture measured at this temperature. **7a**: ^{1}H NMR (400 MHz, −70 °C, acetone-d_6) δ −15.37 (s, 1H, Ru−H), 2.06 (obscured by the residual proton signal of acetone-d_6, C$_5$$Me_5$), 2.08 (s, 15H, C$_5$$Me_5$), 2.27_1 (s, 3H, μ_3-η^3-C$_3$H$_2$$Me$), 9.18 (s, 2H, μ_3-η^3-C$_3$$H_2$Me), 16.69 (s, 1H, μ_3-CH); ^{13}C NMR (100 MHz, −70 °C, acetone-d_6) δ 10.5 (q, J_{CH} = 128.3 Hz, C$_5$$Me_5$), 10.8 (q, J_{CH} = 127.5 Hz, C$_5$$Me_5$), 30.7 (obscured by the signal of acetone-d_6, μ_3-η^3-C$_3$H$_2$$Me$), 104.7 (s, C_5Me$_5$), 105.1 (s, C_5Me$_5$), 132.1 (s, μ_3-η^3-CHCMeCH−), 171.8 (d, J_{CH} = 196.9 Hz, μ_3-η^3-CHCMeCH−), 356.3 (d, J_{CH} = 166.8 Hz, μ_3-CH). **7b**: ^{1}H NMR (400 MHz, −70 °C, acetone-d_6) δ −15.00 (br s, 1H, Ru−H), 2.26_5 (s, 3H, μ_3-η^3-C$_3$H$_2$$Me$), 6.89 (dd, J_{HH} = 2.4, 2.4 Hz, 1H, μ_3-η^3-C$_3$$H$HMe), 9.27 (d, J_{HH} = 2.4 Hz, 1H, μ_3-η^3-C$_3$HHMe), 16.78 (s, 1H, μ_3-CH) (the ^{1}H signals of the C$_5$Me$_5$ groups of **7b** were obscured by the residual proton signals of acetone-d_6 and the C$_5$Me$_5$ signals of **7a**); ^{13}C NMR (100 MHz, −70 °C, acetone-d_6) δ 10.4 (C$_5$$Me_5$), 10.7 (C$_5$$Me_5$), 104.5 (s, C_5-

Me$_5$), 105.1 (s, *C*$_5$Me$_5$), 105.2 (s, *C*$_5$Me$_5$) (other ^{13}C signals of **7b** were not observed, due to low distribution of **7b** in the solution); IR (ATR, cm^{-1}) 834, 1023, 1075, 1108, 1376, 1424, 1451, 1480, 2925, 2965. Anal. Calcd for $C_{35}H_{52}F_{12}P_2Ru_3$: C, 39.44; H, 4.92. Found: C, 40.03; H, 4.95. Since the solvent could not be removed from the dicationic mixture completely, the data of carbon analysis for the mixture did not fit well with the calculated value. An attempt to obtain ESI mass spectra for the dicationic mixture **7a**,**b** resulted in deprotonation during ionization, and the same spectrum as for **8** was obtained.

Preparation of (Cp*Ru)$_3$(μ_3-CH)(μ_3-η^1:η^3:η^1-CHCHCH)(μ-H) (5b). Heptane (10 mL) and the μ_3-η^1:η^3:η^1-allyl complex (Cp*Ru)$_3$(μ_3-η^1:η^3:η^1-CHCHCMe)(μ-H)$_4$[7] (56.2 mg, 0.073 mmol) were charged in a glass autoclave. The reaction solution was then heated to 180 °C for 6 days. After the solvent was evaporated under reduced pressure, the residual solid was dissolved in 3 mL of toluene. The product was purified by the use of column chromatography on neutral alumina (Merck Art. No. 1097) with toluene. The first reddish brown band was collected, and removal of the solvent under reduced pressure afforded 32.0 mg of **5b** as a red solid (0.042 mmol; 57%). ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$): δ -22.07 (d, $J_{HH} = 3.2$ Hz, 1H, Ru$-$*H*), 1.55 (s, 15H, C$_5$*Me*$_5$), 1.90 (s, 30H, C$_5$*Me*$_5$), 5.73 (dd, $J_{HH} = 3.2$, 5.6 Hz, 1H, μ_3-η^1:η^3:η^1-CHC*H*CH), 8.50 (d, $J_{HH} = 5.6$ Hz, 2H, μ_3-η^1:η^3:η^1-C*H*CHC*H*), 16.12 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 25 °C, benzene-*d*$_6$): δ 11.2 (q, $J_{CH} = 126.1$ Hz, C$_5$Me$_5$), 11.8 (q, $J_{CH} = 125.1$ Hz, C$_5$Me$_5$), 91.4 (s, C$_5$Me$_5$), 93.2 (s, C$_5$Me$_5$), 101.8 (d, $J_{CH} = 158.0$ Hz, μ_3-η^1:η^3:η^1-CH*C*HCH), 175.6 (d, $J_{CH} = 133.7$ Hz, μ_3-η^1:η^3:η^1-*C*HCH*C*H), 324.7 (d, $J_{CH} = 158.0$ Hz, μ_3-*C*H). IR (ATR, cm^{-1}): 877, 1025, 1372, 1453, 1473, 11556, 2894, 2964. Anal. Calcd for $C_{34}H_{50}Ru_3$: C, 53.59; H, 6.61. Found C, 53.53; H, 6.83.

Preparation of [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^3-C$_3$H$_3$)(μ-H)]$^+$ (7c). Toluene (10 mL) and (Cp*Ru)$_3$(μ_3-CH)(μ_3-η^1:η^3:η^1-CHCHCH)(μ-H) (**5b**; 34.4 mg, 0.0450 mmol) were charged in a 50 mL reaction flask. After [Cp$_2$Fe](PF$_6$) (29.2 mg, 0.0882 mmol) was added to the solution at room temperature, the solution was vigorously stirred for 2 h. The solution turned from red to brown and formed a brown precipitate. The precipitate was separated by removal of the supernatant including ferrocene. The brown solid was rinsed three times with 5 mL of toluene. The residual solid was dried under reduced pressure, and 32.3 mg of the hexafluorophosphate salt of **7c** was obtained as a brown solid (0.042 mmol, 94%). ^{1}H NMR (400 MHz, -70 °C, acetone-*d*$_6$): δ -15.05 (br s, 1H, Ru$-$*H*), 2.08 (s, 30H, C$_5$*Me*$_5$), 2.11 (s, 15H, C$_5$*Me*$_5$), 7.04 (brd, 1H, $J_{HH} = 3.2$ Hz, μ_3-η^3-CHC*H*CH$-$), 9.24 (br d, $J_{HH} = 2.4$ Hz, 2H, μ_3-η^3-C*H*CHC*H*$-$), 16.65 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, -70 °C, acetone-*d*$_6$): δ 10.7 (q, $J_{CH} = 128.3$ Hz, C$_5$*Me*$_5$), 10.8 (q, $J_{CH} = 128.2$ Hz, C$_5$*Me*$_5$), 104.9 (s, *C*$_5$Me$_5$), 105.4 (s, *C*$_5$Me$_5$), 116.4 (d, $J_{CH} = 209.1$ Hz, μ_3-η^3-CH*C*HCH$-$), 166.1 (d, $J_{CH} = 198.8$ Hz, μ_3-η^3-*C*HCH*C*H$-$), 355.8 (d, $J_{CH} = 174.5$ Hz, μ_3-CH). IR (ATR, cm^{-1}): 837, 1023, 1378, 1425, 1451, 1474, 2913, 2964. Since the solvent could not be removed from the dicationic complex completely, the data of carbon analysis for **7c** did not fit well with the calculated value. An attempt to obtain ESI mass spectra for the dicationic complex **7c** also resulted in deprotonation during ionization, as found in the dicationic mixture **7a**,**b**.

Preparation of [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^3-C$_3$H$_2$Me)]$^+$ (8). Acetone (10 mL) and the dicationic mixture of hexafluorophosphate salts of [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^3-C$_3$H$_2$Me)(μ-H)]$^{2+}$ (**7a**,**b**; 135.4 mg, 0.13 mmol) were charged in a 50 mL reaction flask. After 3 equiv of triethylamine (40 μL) was added to the solution at room temperature, the solution was vigorously stirred for 2 h. The solution turned from brown to brownish yellow. After the solvent was removed under reduced pressure, the residual brownish yellow solid was then dissolved in 2 mL of THF. The product was purified by the use of column chromatography on alumina (Merck Art. No. 1097) with THF. The yellow band was collected, and removal of the solvent in vacuo afforded 103.3 mg of the hexafluorophosphate salt of **8** as a yellow crystalline solid (0.11 mmol; 70%). A single crystal suitable for diffraction studies was prepared from a cold THF solution of a tetraphenylborate salt of **8**, which was obtained by the anion exchange of PF$_6$$^-$ with BPh$_4$$^-$ using an excess amount of NaBPh$_4$. ^{1}H NMR (400 MHz, 23 °C, acetone-*d*$_6$): δ 1.84 (s, 30H, C$_5$*Me*$_5$), 1.86 (s, 15H, C$_5$*Me*$_5$), 2.58 (s, 3H, μ_3-η^3-C$_3$H$_2$*Me*), 7.77 (s, 2H, μ_3-η^3-C$_3$*H*$_2$Me), 17.08 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 23 °C, acetone-*d*$_6$): δ 10.9 (q, $J_{CH} = 127.4$ Hz, C$_5$*Me*$_5$), 11.2 (q, $J_{CH} = 127.5$ Hz, C$_5$*Me*$_5$), 30.5 (obscured by the residual proton signal of acetone-*d*$_6$; μ_3-η^3-C$_3$H$_2$*Me*), 98.5 (s, *C*$_5$Me$_5$), 109.9 (s, *C*$_5$Me$_5$), 158.2 (d, $J_{CH} = 189.1$ Hz, μ_3-η^3-*C*HCMe*C*H$-$), 162.6 (s, μ_3-η^3-CH*C*MeCH$-$), 354.5 (d, $J_{CH} = 165.6$ Hz, μ_3-*C*H). IR (ATR, cm^{-1}): 835, 876, 1023, 1071, 1105, 1262, 1376, 1425, 1451, 1474, 2910, 2964. Anal. Calcd for $C_{35}H_{51}F_6PRu_3$: C, 45.70; H, 5.59. Found: C, 45.09; H, 5.59. Although the data of the carbon analysis did not fit with the calculated value in spite of several attempts, the composition of the cationic moiety of **8** was confirmed by the ESI-MS spectrum. ESI-MS(+) (*m/z* (relative intensity)): 777 (100) (calcd for $C_{35}H_{51}Ru_3^+$, 777).

Protonation of the Monocationic Complex 8. The hexafluorophosphate salt of **8** (15.2 mg, 0.014 mmol) and dichloromethane-*d*$_2$ (0.4 mL) were charged in an NMR tube. After an excess amount of trifluoromethanesulfonic acid was added to the solution at room temperature, the solution was vigorously stirred for 10 min. Formation of the dicationic mixture **7a**,**b** was confirmed by the ^{1}H NMR spectra. ^{1}H NMR (400 MHz, 23 °C, dichloromethane-*d*$_2$): δ -15.48 (br, Ru$-$*H*), 7.91 (br, μ_3-C$_3$*H*$_2$Me), 15.81 (br, μ_3-C*H*).

Reduction of the Dicationic Mixture 7a,b. The mixture of hexafluorophosphate salts of the dicationic complexes **7a**,**b** (30.3 mg, 0.028 mmol) and THF (10 mL) were charged in a reaction flask. A 0.5 M DME solution of sodium naphthalenide (0.15 mL, 0.26 mmol) was then added to the solution at 25 °C. While complexes **7a**,**b** were suspended in the solvent at the beginning, they gradually dissolved. The solution was allowed to react for 2 h with vigorous stirring, and it turned red. After the solvent was removed under reduced pressure, the product was dissolved in 3 mL of toluene and purified by the use of column chromatography on alumina (Merck Art. No. 1097) with toluene. Removal of the solvent in vacuo afforded 20.7 mg of the mixture **5a**,**c** as a red solid (94% yield). The ratio between **5a** and **5c** was estimated as 65:35 by the ^{1}H NMR spectrum. Formation of **5a** was confirmed by comparing its ^{1}H NMR spectrum with that of an authentic sample prepared by the method described in ref 10. **5c**: ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$) δ -22.77 (d, $J_{HH} = 4.0$ Hz, 1H, Ru$-$*H*), 1.52 (s, 15H, C$_5$*Me*$_5$), 1.83 (s, 15H, C$_5$*Me*$_5$), 1.88 (s, 15H, C$_5$*Me*$_5$), 2.44 (s, 3H, μ_3-C*Me*CHCH), 5.43 (dd, $J_{HH} = 5.6$, 4.0 Hz, 1H, μ_3-CMeC*H*CH), 8.48 (d, $J_{HH} = 5.6$ Hz, 1H, μ_3-CMeCHC*H*), 16.40 (s, 1H, μ_3-C*H*); ^{13}C NMR (100 MHz, 25 °C, benzene-*d*$_6$) δ 10.9 (q, $J_{CH} = 125.9$ Hz, C$_5$*Me*$_5$), 11.4 (q, $J_{CH} = 125.6$ Hz, C$_5$*Me*$_5$), 11.7 (q, $J_{CH} = 125.0$ Hz, C$_5$*Me*$_5$), 35.6 (q, $J_{CH} = 122.2$ Hz, μ_3-C*Me*CHCH), 91.1 (s, *C*$_5$Me$_5$), 93.5 (s, *C*$_5$Me$_5$), 93.6 (s, *C*$_5$Me$_5$), 104.4 (d, $J_{CH} = 155.0$ Hz, μ_3-CMe*C*HCH), 177.2 (d, $J_{CH} = 140.3$ Hz, μ_3-CMeCH*C*H), 183.2 (s, μ_3-*C*MeCHCH), 326.5 (d, $J_{CH} = 157.1$ Hz, μ_3-*C*H).

Preparation of [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^1:η^3:η^1-CHCMeCH)(μ-Cl)]$^{2+}$ (10). Hexafluorophosphate salts of the dicationic complexes [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^3-C$_3$H$_2$Me)(μ-H)]$^{2+}$ (**7a**,**b**; 78.1 mg, 0.073 mmol) and dichloromethane (5 mL) were charged in a sealed tube. The solution was vigorously stirred for 12 h at 100 °C. The solution turned from brown to green. Removal of the solvent under reduced pressure afforded a mixture of hexafluorophosphate salts of [(Cp*Ru)$_3$(μ_3-CH)(μ_3-CHCMeCH)(μ-Cl)]$^{2+}$ (**10**) and the monocationic complex **8** in a ratio of 74:26 (determined by ^{1}H NMR). The residual solid was rinsed three times with 2 mL of THF to remove **8**. The residual solid was dried under reduced pressure, and 7.7 mg of the hexafluorophosphate salt of **10** was obtained as a green solid (10% yield). A single crystal of **10-PF$_6$** suitable for the X-ray diffraction studies was obtained from the dichloromethane solution of the mixture of **10** and **8** at −30 °C. X-ray crystallography showed that one dichloromethane molecule was contained in the unit cell. Elemental analysis was measured for this single crystal, which contained a crystallizing solvent. ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ 1.97 (s, 15H, C$_5$*Me*$_5$), 2.04 (s, 30H, C$_5$*Me*$_5$), 2.47 (s, 3H, μ_3-CHC*Me*CH), 10.09 (s, 2H, μ_3-C*H*CMeC*H*), 15.01 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 23 °C, acetone-d_6): δ 11.0 (q, $J_{\rm CH}$ = 128.6 Hz, C$_5$*Me*$_5$), 11.2 (q, $J_{\rm CH}$ = 128.6 Hz, C$_5$*Me*$_5$), 21.3 (q, $J_{\rm CH}$ = 128.6 Hz, μ_3-CHC*Me*CH), 105.9 (s, *C*$_5$Me$_5$), 110.0 (s, *C*$_5$Me$_5$), 112.6 (s, μ_3-CH*C*MeCH), 195.4 (d, $J_{\rm CH}$ = 166.7 Hz, μ_3-*C*HCMe*C*H), 330.8 (d, $J_{\rm CH}$ = 173.8 Hz, μ_3-*C*H). IR (ATR, cm^{-1}): 832, 875, 1020, 1079, 1114, 1381, 1432, 1460, 1493, 2913, 2971, 3001. Anal. Calcd for $C_{36}H_{53}Cl_3F_{12}P_2Ru_{3-}$: C, 36.48; H, 4.51. Found: C, 36.67; H, 4.49.

Preparation of [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^1:η^3:η^1-CHCMeCH)(μ-CO)]$^+$ (11). Dichloromethane (5 mL) and hexafluorophosphate salts of the dicationic complexes [(Cp*Ru)$_3$(μ_3-CH)(μ_3-CHCMeCH)(μ-H)]$^{2+}$ (**7a**,**b**; 78.1 mg, 0.073 mmol) were charged in a 50 mL reaction flask. The reaction flask was then degassed, and 1 atm of CO was subsequently introduced at −78 °C. The reaction flask was gradually warmed to 25 °C and vigorously stirred for 24 h. The solution turned from brown to yellow. The reaction solution was evaporated under reduced pressure. The residual solid was dissolved in THF, and the product was purified by the use of column chromatography on alumina (Merck Art.) with THF and MeOH. The hexafluorophosphate salt of **11** was obtained as a dark yellow solid on removal of the solvent under reduced pressure (65.1 mg, 96%). The tetraphenylborate salt of **11** was obtained by the treatment of the hexafluorophosphate salt of **11** (65.1 mg, 0.071 mmol) with an excess amount of NaBPh$_4$ (75.1 mg, 0.22 mmol) in 10 mL of methanol. A dark yellow solid was immediately formed, and the precipitate was rinsed three times with 2 mL of methanol. The precipitate was then dried under reduced pressure, and 73.3 mg of tetraphenylborate salt of **11** was obtained as a yellow solid (92%). **11-PF$_6$**: ^{1}H NMR (400 MHz, 23 °C, acetone-d_6) δ 1.83 (s, 15H, C$_5$*Me*$_5$), 1.89 (s, 30H, C$_5$*Me*$_5$), 2.34 (s, 3H, μ_3-CHC*Me*CH), 8.55 (s, 2H, μ_3-C*H*CMeC*H*), 15.50 (s, 1H, μ_3-C*H*); ^{13}C NMR (100 MHz, 23 °C, acetone-d_6) δ 10.3 (q, $J_{\rm CH}$ = 126.9 Hz, C$_5$*Me*$_5$), 11.1 (q, $J_{\rm CH}$ = 126.9 Hz, C$_5$*Me*$_5$), 21.6 (q, $J_{\rm CH}$ = 124.6 Hz, μ_3-CHC*Me*CH), 99.1 (s, *C*$_5$Me$_5$), 103.0 (s, *C*$_5$Me$_5$), 106.6 (s, μ_{3-}CH*C*MeCH), 182.4 (d, $J_{\rm CH}$ = 146.5 Hz, μ_3-*C*HCMe*C*H), 239.6 (s, μ-*C*O), 326.1 (d, $J_{\rm CH}$ = 165.6 Hz, μ_3-*C*H); IR (ATR, cm^{-1}): 836, 1024, 1375, 1456, 1786 ($\nu_{\rm CO}$), 2905. **11-BPh$_4$**: ^{1}H NMR (400 MHz, 23 °C, acetone-d_6) δ 1.83 (s, 15H, C$_5$*Me*$_5$), 1.89 (s, 30H, C$_5$*Me*$_5$), 2.33 (s, 3H, μ_3-CHC*Me*CH), 6.76 (t, $J_{\rm HH}$ = 7.2 Hz, 4H, *p*-B*Ph*$_4$), 6.91 (dd, $J_{\rm HH}$ = 7.2, 7.2 Hz, 8H, *m*-B*Ph*$_4$), 7.33, (m, 8H, *o*-B*Ph*$_4$), 8.56 (s, 2H, μ_3-C*H*CMeC*H*), 15.49 (s, 1H, μ_3-C*H*). Anal. Calcd for $C_{60}H_{71}BORu_3$: C, 64.22; H, 6.38. Found: C, 63.63; H, 6.49. Although the data of carbon analysis for **11-BPh$_4$** did not fit well with the calculated value in spite of several attempts, the composition of the cationic moiety of **11-BPh$_4$** was confirmed by an ESI-MS spectrum. ESI-MS(+) (*m/z* (relative intensity)): 804 (100) (calcd for $C_{36}H_{51}ORu_3^+$, 804).

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Supporting Information Available: Results of the X-ray diffraction studies and CIF files giving crystallographic data for **8-BPh$_4$**, **10-PF$_6$**, and **11-BPh$_4$** and text and a figure giving the results of a kinetic study on the deprotonation of the dicationic mixture **7a**,**b** in acetone/methanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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