Synthesis and Structure of Cationic Triruthenium Complexes Containing an Oxametallacycle: Reversible Carbon−Oxygen Bond Formation and Scission on an Electron-Deficient Triruthenium Plane

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A trimetallic μ-hydroxo complex, $[(Cp^*Ru)_3(\mu\text{-OH})(\mu_3\text{-CH})(\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-CHCMeCH})]^{2+}$ (**6**), was obtained by the reaction of an equilibrating mixture of the dicationic tris(μ-carbene) complexes $[(Cp^*Ru)_3(\mu_3\text{-CH})(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-}C_3MeH_2)]^{2+}$ (**4a** and **4b**) with water. Treatment of the μ-hydroxo complex with a base affords a novel μ_3-2-oxa-4-methylruthenacyclopentenyl complex, $[(Cp^*Ru)_3(\mu_3\text{-CH})\{\mu_3\text{-OC(H)C(Me)CH}-\}]^{2+}$ (**8**), as a result of reductive C−O bond coupling. Complex **8** underwent unprecedented isomerization to a μ_3-2-oxa-3-methylruthenacyclopentenyl complex, $[(Cp^*Ru)_3(\mu_3\text{-CH})\{\mu_3\text{-O-C(Me)C(H)CH}-\}]^{2+}$ (**8**), containing a methyl group at the 3-position of the oxaruthenacycle moiety upon heating, which involves sequential C−O bond cleavage and re-formation via the formation of a transient μ-oxo complex having a μ_3-η^3-C_3 ring on the triruthenium plane.

Introduction

Oxidative addition of water is highly relevant to a variety of catalytic processes such as water−gas shift[1] and olefin/nitrile hydration.[2] Since an O−H bond scission is regarded as an initial step of the catalytic process, hydrido−hydroxo complexes formed by the reaction of transition metal complexes with water have so far attracted considerable attention.[3,4] However, reactivity of the resulting hydroxo group with the hydrocarbyl ligand has been scarcely investigated,[5] although this is a key step of the functionalization of hydrocarbons.[4g,6]

We have studied the reactivity of a triruthenium pentahydrido complex, $\{Cp^*Ru(\mu\text{-H})\}_3(\mu_3\text{-H})_2$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$), with various hydrocarbons including alkane, so far.[7] The reaction of **1** with cyclopentadiene afforded a *nido*-ruthenacyclopentadiene complex **2** as a result of $C(sp^2)-C(sp^3)$ bond cleavage induced by the cooperative action of the neighboring ruthenium centers (Scheme 1).[8] Further C−C bond cleavage was observed on heating **2** at 140 °C, and a μ_3-methylidyne-μ_3-η^3-diruthenaallyl complex, $(Cp^*Ru)_3(\mu_3\text{-CH})(\mu_3\text{-}\eta^3\text{-CHCMeCH})(\mu\text{-H})$ (**3**), was obtained in high yield.[9] Although this reaction implies the high potential of a cluster compound in activating molecules, attempts to introduce a functional group into **3** by the reaction of water or other nucleophiles were unsuccessful due to the robustness of **3** toward air and moisture. In order to enhance the reactivity with nucleophiles such as water, we examined the chemical oxidation of **3** and obtained a mixture of hexafluorophosphate salts of the dicationic complexes **4a** and **4b** by two-electron oxidation (Scheme 2).[10] The diruthenaallyl skeleton of **3** was transformed to the μ_3-η^3-C_3 ring structure upon oxidation. The most striking feature of the μ_3-η^3-C_3 ring structure found in the monocationic complex $[(Cp^*Ru)_3(\mu_3\text{-CH})(\mu_3\text{-}\eta^3\text{-}C_3MeH_2)]^+$ (**5**), which was obtained by deprotonation from the dicationic mixture **4a** and **4b**, is the extremely long C−C bond distances (average of the three C−C distances was 1.60 Å). The DFT calculations showed that the μ_3-η^3-C_3 ligand was a resonance hybrid between the tris(μ-carbene) and the μ_3-cyclopropenyl structure.[11] The J_{C-H} value of 196 Hz observed for the ring carbon of **4a** strongly implied the carbenic character of the ring carbon.

(1) (a) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941−3942. (b) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027−2038.

(2) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188. (b) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030−3031. (c) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723−729.

(3) (a) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387−6389. (b) Yoon, M.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1997**, 639−640. (c) Tani, K.; Iseki, A.; Yamagata, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 3381−3383. (d) Dorta, R.; Togni, A. *Organometallics* **1998**, *17*, 3423−3428. (e) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144−1147. (f) Dorta, R.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Chem.−Eur. J.* **2003**, *9*, 5237−5249.

(4) (a) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. (A)* **1968**, 2859−2864. (b) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472−5478. (c) Gotzig, J.; Werner, R.; Werner, W. *J. Organomet. Chem.* **1985**, *285*, 99−114. (d) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875−5876. (e) Ho, W. G.-Y.; Wong, W.-T. *Polyhedron* **1995**, *14*, 2849−2855. (f) Chérioux, F.; Maisse-François, A.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *Dalton Trans.* **2001**, 2184−2187. (g) Faure, M.; Vallina, A. T.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **2001**, *621*, 103−108. (h) Jazzar, R. F. R.; Bhatia, P. H.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2003**, *22*, 670−683.

(5) (a) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603−1604. (b) Bryndza, H. E. *Organometallics* **1985**, *4*, 406−408.

(6) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*: University Science Books: Mill Valley, CA, 1987. (b) Crabtree. R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.: Wiley: New York, 2001.

(7) Suzuki, H. *Eur. J. Inorg. Chem.* **2002**, 1009−1023.

(8) (a) Suzuki, H.; Takaya, Y.; Takemori, T.; Tanaka, M. *J. Am. Chem. Soc.*, **1994**, *116*, 10779−10780. (b) Khoroshun, D. V.; Inagaki, A.; Suzuki, H.; Vyboishchikov, S. F.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **2003**, *125*, 9910−9911.

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

(10) Takao, T.; Moriya, M.; Suzuki, H. *Organometallics* **2007**, *26*, 1349−1360.

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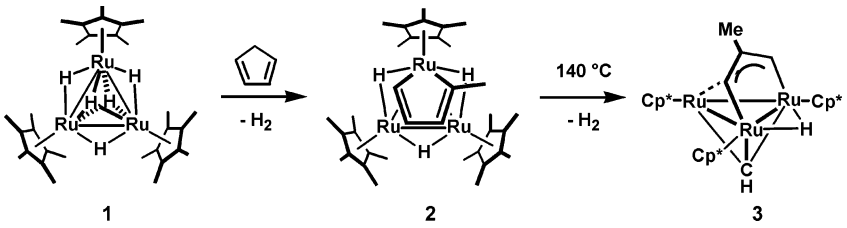
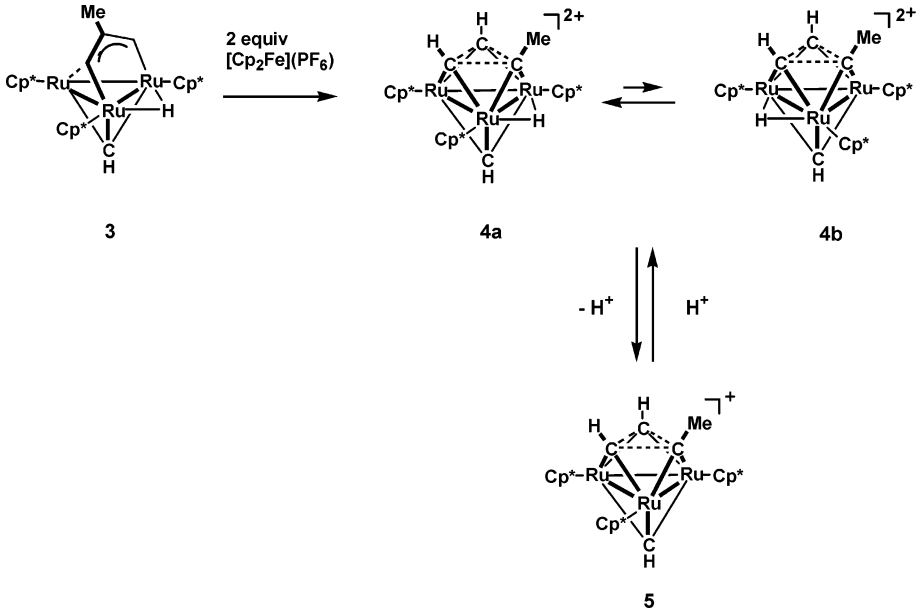
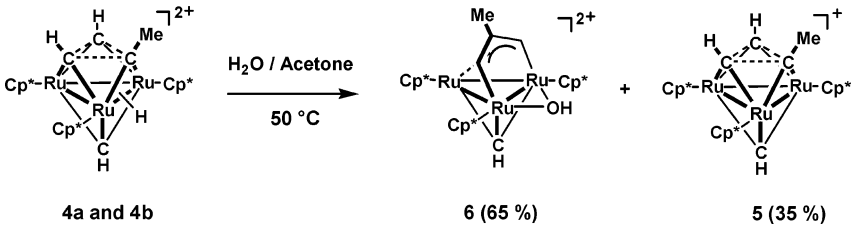
Scheme 1



Scheme 2



Scheme 3



Complex **4** contains highly charged ruthenium centers, and this caused spontaneous liberation of the hydrido ligand as a proton to generate the monocationic complex **5**. It is anticipated that such highly charged metal centers would increase the reactivity toward nucleophiles. We report herein a carbon−oxygen bond formation on the electron-deficient metal centers via a μ-hydroxo complex by the reaction of **4** with water. A novel skeletal rearrangement of the obtained oxaruthenacycle by way of sequential C−O bond cleavage and re-formation is also mentioned.

Results and Discussion

The dicationic complexes **4a** and **4b** immediately reacted with water at room temperature to form a dicationic μ-hydroxo complex, $[(Cp^*Ru)_3(\mu\text{-OH})(\mu_3\text{-CH})(\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-CHCMeCH})]^{2+}$ (**6**), and **5** in 27 and 73% yield, respectively (Scheme 3). Complex **6** is formed by way of a nucleophilic addition of water to **4**, and **5** is formed via deprotonation from **4**. The yield of **6** was increased along with raising the reaction temperature, and the yield reached 65% at 50 °C.

Apparently, nucleophilic attack of water at the metal center followed by the elimination of dihydrogen occurred during the reaction, and this was accompanied by the skeletal rearrangement of the μ_3-η^3-C_3 ring to the diruthenaallyl skeleton. Due to the electron deficiency of the cationic ruthenium centers, the acidity of the coordinated water should increase. This would facilitate proton transfer from the coordinated water to the hydrido ligand. Therefore, complex **6** was probably formed by way of proton transfer rather than oxidative addition of water, which was often observed for a low-valent metal center, such as Ir(I).[3] The fact that **6** was obtained as a single isomer having the 2-methyldiruthenaallyl structure indicates that the carbon−carbon bond was selectively cleaved at the C(H)−C(H) position.

A single crystal of the tetrafluoroborate salt of **6** suitable for the diffraction studies was obtained by changing the counteranion from PF_6^- to BF_4^-. The molecular structure of **6** is shown in Figure 1, and relevant bond lengths and angles are listed in Table 1. Both the hydroxo group and the allylic group bridge Ru(2) and Ru(3), and the molecule has an approximate mirror plane with O(1), C(1), C(3), C(5), and Ru(1) atoms. Notably,

(11) Takao, T.; Inagaki, A.; Murotani, E.; Imamura, T. *Organometallics* **2003**, *22*, 1361−1363.

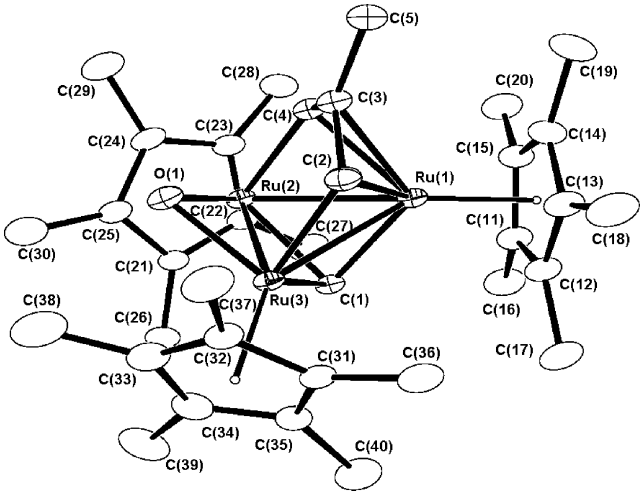


Figure 1. Molecular structure and labeling scheme of **6** with thermal ellipsoids at the 30% probability level. An anionic moiety (BF_4^-) and solvent molecules (H_2O) are omitted for clarity.

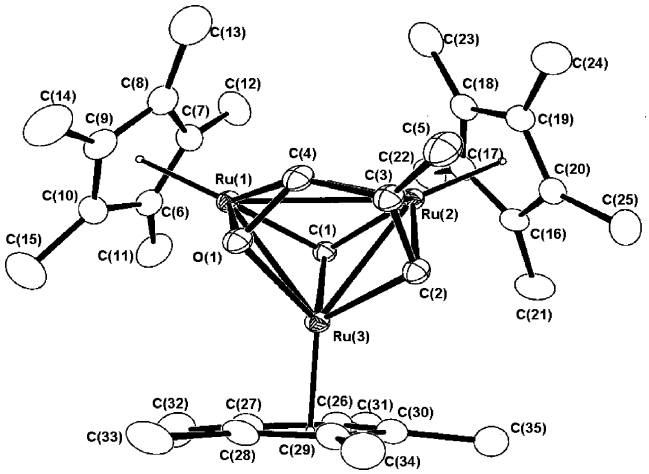


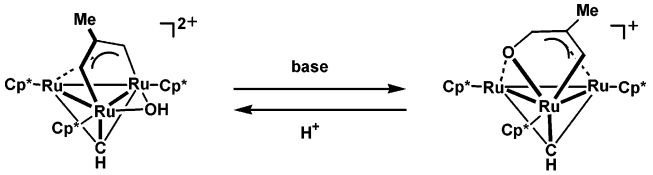
Figure 2. Molecular structure and labeling scheme of **8** with thermal ellipsoids at the 30% probability level. An anionic moiety (BPh_4^-) is omitted for clarity.

the hydroxo and the diruthenaallyl groups were located on the opposite face of the μ_3-methylidyne group with respect to the Ru_3 plane. Structural parameters of **6** are similar to those found in the dicationic μ_3-diruthenaallyl complex, $[(Cp^*Ru)_3(\mu\text{-Cl})(\mu_3\text{-CH})(\mu_3\text{-}\eta^3\text{-CHCMeCH})]^{2+}$ (**7**), which was obtained by the reaction of **4** with CH_2Cl_2.[10]

The ^1H and ^{13}C signals of the allylic moiety of **6** shifted downfield by comparison with those of the corresponding neutral diruthenaallyl complex **3**. A singlet signal of the proton attached to the α-carbons appeared at δ 10.09 in the ^1H NMR spectrum of **6**. While that of the dicationic **7** appeared at the same shift (δ 10.09),[10] that of **3** appeared at a higher magnetic field (δ 8.24).[9] Thus, the downfield shift is probably due to the deshielding effect induced by the dicationic metal centers. The ^{13}C signal of the α-carbons (δ 194.1) also shifted downfield compared to that of **3** (δ 174.6).[9]

The presence of the μ-hydroxo group was unambiguously ascertained by the ^1H NMR spectrum, although the stretching vibration of the μ-hydroxo group was not clear in the IR spectrum.[12] The signal assignable to the hydroxy group appeared at δ 8.58 as a singlet, which completely disappeared upon addition of D_2O. The chemical shift of δ 8.58 was significantly lower than those reported for the triosmium μ-hydroxo clusters, $Os_3(\mu\text{-H})(\mu\text{-OH})(CO)_{10-n}L_n$ (δ −1.6 to 0.4).[4] This is probably due to the dicationic nature of **6**.

Scheme 4



6 **8**

Actually, treatment of **6** with triethylamine resulted in deprotonation from the hydroxy group, and the monocationic 2-oxaruthenacycle complex $[(Cp^*Ru)_3(\mu_3\text{-CH})\{\mu_3\text{-OC(H)C(Me)CH}-\}]^+$ (**8**) was quantitatively formed (Scheme 4). A C−O bond was formed between the diruthenaallyl and the μ-hydroxo groups, which are mutually positioned in *cis* geometry. This reaction shown in Scheme 4 is reversible. The C−O bond was readily cleaved upon treatment of **8** with $HBF_4{\cdot}OEt_2$ or CF_3COOH, and complex **6** was quantitatively regenerated. Re-formation of the μ-hydroxo group as a result of C−O bond scission suggests that protonation occurred at the lone-pair electron on the oxygen atom. We have reported similar site-selective protonation at the nitrogen atom in a perpendicularly coordinated benzonitrile complex, $(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-PhCN})(\mu\text{-H})_2(\mu_3\text{-H})$,[13a] and a face-capping μ_3-pyridine complex, $(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_5H_5N)(\mu\text{-H})_3$,[13b] respectively.

An X-ray diffraction study clearly demonstrates the oxaruthenacycle skeleton of **8** (Figure 2). Relevant bond lengths and angles of **8** are listed in Table 2. Although there have been a few examples containing a μ-[14] or a μ_3-2-oxametallacyclopentenyl ligand,[15] it is noteworthy that the 2-oxaruthenacyclopentyl skeleton in **8** was a very rare example of C−O bond formation by reductive coupling between the μ_3-diruthenaallyl moiety and the μ-hydroxo group. Formation of **8** represents a novel method to introduce a functional group into a hydrocarbyl ligand using a cationic cluster. We have previously shown a similar type of functionalization of hydrocarbons by the reaction of $\{Cp^*Ru(\mu_3\text{-OH})\}_4$ with activated alkynes.[16]

The C(4)−O(1) distance of 1.380(2) Å lies between the C−O single bond (1.43 Å) and the C═O double bond (1.23 Å). The oxacycle is regarded as a coordinated methacrolein on the Ru_3 plane. The ^{13}C signal assignable to C(4), which is next to the oxygen atom, was observed at δ 84.3 as a doublet (J_{C-H} = 180.7 Hz). The relatively large J_{C-H} value is quite consistent with that found for aldehydes.

The C(2)−C(3) and C(3)−C(4) lengths of 1.413(2) and 1.414(3) Å, respectively, indicate that there still remains some allylic character among the C(2), C(3), and C(4) atoms. In addition, the ^{13}C signal of the C(2) appeared at δ 176.2 (d, J_{C-H} = 164.9 Hz), and the shift is characteristic for the μ-carbene ligand.

(12) A broad absorption was observed at 3545 cm^{-1} in the IR spectrum of **6**. However, we could not assign the signal to the μ-OH group or the lattice water since a single crystal of **6** contains three molecules of water.

(13) (a) Takao, T.; Kawashima, T.; Matsubara, K.; Suzuki, H. *Organometallics* **2005**, *24*, 3371−3374. (b) Kawashima, T.; Takao, T.; Suzuki, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 7615−7618.

(14) (a) Lin, R. C.; Chi, Y.; Peng, S. M.; Lee, G. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1705−1707. (b) Terada, M.; Higashihara, G.; Inagaki, A.; Akita, M. *Chem. Commun.* **2003**, 2984−2985.

(15) (a) Rybin, L. V.; Osintseva, S. V.; Petrovskii, P. V.; Rybinskaya, M. I.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1994**, *479*, C25−C27. (b) Rybin, L. V.; Osintseva, S. V.; Rybinskaya, M. I.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1995**, *485*, 253−255.

(16) Oshima, M.; Kobayashi, M.; Tanaka, M.; Suzuki, H. *Chem. Lett.* **1995**, 921−922.

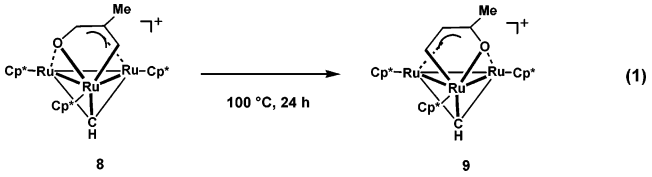
Table 1. Selected Bond Distances (Å) and Angles (deg) for 6

Ru(1)−Ru (2)	2.7085(8)	Ru(1)−Ru(3)	2.7200(7)	Ru(1)−C(1)	2.004(7)
Ru(1)−C(2)	2.134(7)	Ru(1)−C(3)	2.261(7)	Ru(1)−C(4)	2.127(7)
Ru(2)−Ru(3)	2.6254(7)	Ru(2)−C(1)	2.029(6)	Ru(2)−C(4)	2.018(7)
Ru(2)−O(1)	2.038(5)	Ru(3)−C(1)	2.024(6)	Ru(3)−C(2)	2.030(7)
Ru(3)−O(1)	2.035(5)	C(2)−C(3)	1.431(9)	C(3)−C(4)	1.405(10)
C(3)−C(5)	1.511(10)				
Ru(2)−Ru(1)−Ru(3)	57.845(19)	Ru(2)−Ru(1)−C(1)	48.19(17)	Ru(3)−Ru(1)−C(1)	47.84(18)
C(2)−Ru(1)−C(3)	37.9(3)	C(3)−Ru(1)−C(4)	37.2(3)	Ru(1)−Ru(2)−Ru(3)	61.30(2)
Ru(1)−Ru(2)−C(1)	47.43(19)	Ru(1)−Ru(2)−O(1)	97.25(16)	Ru(1)−Ru(2)−C(4)	50.97(19)
Ru(3)−Ru(2)−C(1)	49.56(18)	Ru(3)−Ru(2)−C(4)	86.69(19)	Ru(1)−Ru(2)−O(1)	97.25(16)
Ru(3)−Ru(2)−O(1)	49.81(14)	Ru(1)−Ru(3)−Ru(2)	60.857(19)	Ru(1)−Ru(3)−C(1)	47.22(19)
Ru(2)−Ru(3)−C(1)	49.70(17)	Ru(2)−Ru(3)−C(2)	87.2(2)	Ru(1)−Ru(3)−O(1)	96.98(15)
Ru(2)−Ru(3)−O(1)	49.93(14)	Ru(2)−O(1)−Ru(3)	80.26(17)	Ru(1)−C(1)−Ru(2)	84.4(2)
Ru(1)−C(1)−Ru(3)	84.9(2)	Ru(2)−C(1)−Ru(3)	80.7(2)	Ru(1)−C(2)−Ru(3)	81.5(3)
Ru(1)−C(2)−C(3)	75.9(4)	Ru(3)−C(2)−C(3)	121.5(5)	Ru(1)−C(3)−C(2)	66.2(4)
Ru(1)−C(3)−C(4)	66.2(4)	Ru(1)−C(3)−C(5)	132.3(6)	C(2)−C(3)−C(4)	116.3(6)
C(2)−C(3)−C(5)	120.9(6)	C(4)−C(3)−C(5)	122.2(6)	Ru(1)−C(4)−Ru(2)	81.5(2)
Ru(1)−C(4)−C(3)	76.6(4)	Ru2)−C(4)−C(3)	123.3(5)		

Table 2. Selected Bond Distances (Å) and Angles (deg) for 8

Ru(1)−Ru(2)	2.87712(18)	Ru(1)−Ru(3)	2.68917(18)	Ru(1)−O(1)	2.0155(12)
Ru(1)−C(1)	1.9537(16)	Ru(1)−C(4)	2.3767(17)	Ru(2)−Ru(3)	2.6807(2)
Ru(2)−C(1)	2.0039(16)	Ru(2)−C(2)	2.0767(17)	Ru(2)−C(3)	2.2334(17)
Ru(2)−C(4)	2.5254(19)	Ru(3)−O(1)	2.1143(11)	Ru(3)−C(1)	2.0635(17)
Ru(3)−C(2)	2.0261(17)	O(1)−C(4)	1.380(2)	C(2)−C(3)	1.413(2)
C(3)−C(4)	1.414(3)	C(3)−C(5)	1.505(2)		
Ru(2)−Ru(1)−Ru(3)	57.460(5)	Ru(2)−Ru(1)−O(1)	78.09(3)	Ru(2)−Ru(1)−C(1)	44.06(5)
Ru(2)−Ru(1)−C(4)	56.50(5)	Ru(3)−Ru(1)−C(1)	49.74(5)	Ru(3)−Ru(1)−O(1)	50.99(3)
Ru(3)−Ru(1)−C(4)	66.64(4)	Ru(1)−Ru(2)−Ru(3)	57.745(5)	Ru(1)−Ru(2)−C(1)	42.68(5)
Ru(1)−Ru(2)−C(2)	93.43(5)	Ru(1)−Ru(2)−C(3)	84.21(5)	Ru(1)−Ru(2)−C(4)	51.70(4)
Ru(3)−Ru(2)−C(1)	49.74(5)	Ru(3)−Ru(2)−C(2)	48.39(5)	Ru(3)−Ru(2)−C(3)	71.23(5)
Ru(3)−Ru(2)−C(4)	64.86(4)	Ru(1)−Ru(3)−Ru(2)	64.795(5)	Ru(1)−Ru(3)−O(1)	47.79(3)
Ru(1)−Ru(3)−C(1)	46.26(4)	Ru(1)−Ru(3)−C(2)	100.41(5)	Ru(2)−Ru(3)−O(1)	81.32(4)
Ru(2)−Ru(3)−C(1)	47.82(4)	Ru(2)−Ru(3)−C(2)	50.03(5)	O(1)−Ru(3)−C(2)	79.64(6)
Ru(1)−O(1)−Ru(3)	81.22(4)	Ru(1)−O(1)−C(4)	104.25(10)	Ru(3)−O(1)−C(4)	86.72(10)
Ru(1)−C(1)−Ru(2)	93.26(7)	Ru(1)−C(1)−Ru(3)	84.00(7)	Ru(2)−C(1)−Ru(3)	82.44(6)
Ru(2)−C(2)−Ru(3)	81.58(6)	Ru(2)−C(2)−C(3)	76.99(11)	Ru(3)−C(2)−C(3)	112.82(12)
Ru(2)−C(3)−C(2)	64.96(10)	Ru(2)−C(3)−C(4)	84.47(11)	Ru(2)−C(3)−C(5)	127.43(15)
C(2)−C(3)−C(4)	112.40(15)	C(2)−C(3)−C(5)	125.44(17)	C(4)−C(3)−C(5)	121.14(17)
Ru(1)−C(4)−Ru(2)	71.80(5)	Ru(1)−C(4)−O(1)	57.85(8)	O(1)−C(4)−C(3)	115.92(16)

In order to eliminate methacrolein or 2-methylpropionaldehyde from the triruthenium core, the reaction of **8** with dihydrogen was carried out. However, it has been shown that complex **8** does not react with H_2 even under forcing conditions. Instead, we found that thermolysis of **8** led to formation of an isomeric oxaruthenacycle complex, $[(Cp^*Ru)_3(\mu_3\text{-CH})\{\mu_3\text{-OC(Me)C(H)C(H)}-\}]^+$ (**9**), as a result of sequential C−O bond cleavage and re-formation.



8 **9**

Thermolysis of **8** at 100 °C for 24 h resulted in quantitative formation of **9** (eq 1). The most arresting feature of this reaction is that the methyl group seemingly migrates from the 4- to the 3-position of the 2-oxaruthenacycle skeleton. The metallacycle was thus transformed from a coordinated methacrolein in **8** to a coordinated methylvinyl ketone in **9**.

The molecular structure of **9** is shown in Figure 3, and relevant bond lengths and angles are listed in Table 3. The structure clearly showed the migration of the methyl group on the oxacycle moiety. Due to the presence of the methyl group at the next position of the oxygen atom, the structural parameters of the oxacycle moiety of **9** were considerably different from those of **8**. The angle around the oxygen atom in **9** (∠Ru(3)−O(1)−C(2)) was 107.0(3)°, while the corresponding angle in **8**, ∠Ru(3)−O(1)−C(4), was much smaller (86.72(10)°). This implied reduction of distortion in the five-membered ring in **9**. This is also clearly seen in the bond lengths between Ru(2) and the carbon atom, to which the methyl group directly bound. The Ru(2)−C(2) distance of 2.522(5) Å in **9** was significantly longer than the Ru(2)−C(3) in **8** (2.2334(17) Å). This means that the steric repulsion between the Cp* group on Ru(2) and the methyl group on the oxacycle moiety was considerably

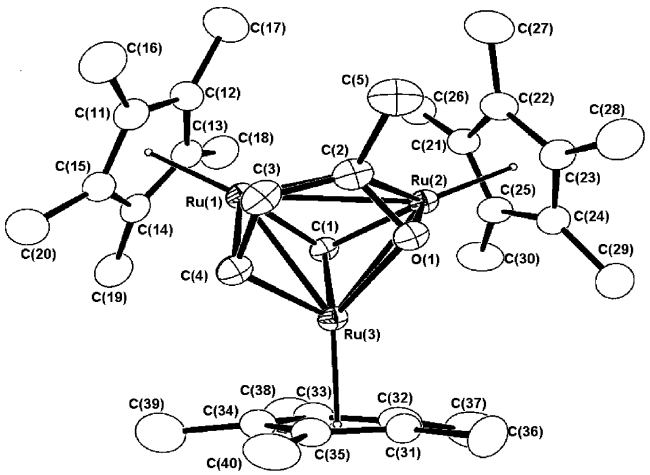


Figure 3. Molecular structure and labeling scheme of **9** with thermal ellipsoids at the 30% probability level. An anionic moiety (PF_6^-) is omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 9

Ru(1)−Ru(2)	2.8985(4)	Ru(1)−Ru(3)	2.6829(4)	Ru(1)−C(1)	2.005(4)
Ru(1)−C(2)	2.540(5)	Ru(1)−C(3)	2.196(4)	Ru(1)−C(4)	2.086(4)
Ru(2)−Ru(3)	2.6931(5)	Ru(2)−O(1)	2.036(3)	Ru(2)−C(1)	1.967(4)
Ru(2)−C(2)	2.522(5)	Ru(3)−O(1)	2.132(3)	Ru(3)−C(1)	2.071(4)
Ru(3)−C(4)	2.022(4)	O(1)−C(2)	1.384(5)	C(2)−C(3)	1.419(8)
C(2)−C(5)	1.502(7)	C(3)−C(4)	1.406(7)		
Ru(2)−Ru(1)−Ru(3)	57.545(11)	Ru(2)−Ru(1)−C(1)	42.61(11)	Ru(2)−Ru(1)−C(2)	54.78(11)
Ru(2)−Ru(1)−C(3)	86.68(14)	Ru(2)−Ru(1)−C(4)	94.54(12)	Ru(3)−Ru(1)−C(1)	49.92(11)
Ru(3)−Ru(1)−C(2)	66.39(10)	Ru(3)−Ru(1)−C(3)	71.38(13)	Ru(3)−Ru(1)−C(4)	48.21(12)
Ru(1)−Ru(2)−Ru(3)	57.204(11)	Ru(1)−Ru(2)−O(1)	75.51(9)	Ru(1)−Ru(2)−C(1)	43.65(11)
Ru(1)−Ru(2)−C(2)	66.46(11)	Ru(3)−Ru(2)−O(1)	51.32(9)	Ru(3)−Ru(2)−C(1)	49.85(11)
Ru(3)−Ru(2)−C(2)	66.46(11)	Ru(1)−Ru(3)−Ru(2)	65.252(12)	Ru(1)−Ru(3)−O(1)	79.17(8)
Ru(1)−Ru(3)−C(1)	47.78(11)	Ru(1)−Ru(3)−C(4)	50.26(12)	Ru(2)−Ru(3)−O(1)	48.22(8)
Ru(2)−Ru(3)−C(1)	46.53(11)	Ru(2)−Ru(3)−C(4)	102.55(14)	O(1)−Ru(3)−C(4)	79.43(17)
Ru(2)−O(1)−Ru(3)	80.46(10)	Ru(2)−O(1)−C(2)	93.0(2)	Ru(3)−O(1)−C(2)	107.0(3)
Ru(1)−C(1)−Ru(2)	93.74(16)	Ru(1)−C(1)−Ru(3)	82.30(14)	Ru(2)−C(1)−Ru(3)	83.62(14)
Ru(1)−C(2)−Ru(2)	69.87(11)	Ru(1)−C(2)−O(1)	100.0(3)	Ru(1)−C(2)−C(3)	59.7(2)
Ru(1)−C(2)−C(5)	130.2(4)	Ru(2)−C(2)−O(1)	53.7(2)	Ru(2)−C(2)−C(3)	125.0(3)
Ru(2)−C(2)−C(5)	106.8(4)	O(1)−C(2)−C(3)	114.2(4)	O(1)−C(2)−C(5)	117.9(5)
Ru(1)−C(3)−C(2)	86.4(3)	Ru(1)−C(3)−C(4)	66.6(2)	C(2)−C(3)−C(4)	115.7(4)
Ru(1)−C(4)−Ru(3)	81.53(16)	Ru(1)−C(4)−C(3)	75.2(3)	Ru(3)−C(4)−C(3)	112.7(3)

reduced in **9**, and this would be a driving force for this isomerization.

The kinetic studies for the isomerization were performed, and temperature dependence of the first-order rate constant (k_1) was used in deriving Arrhenius activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The activation parameters assumed from the first-order rate constant are estimated at $\Delta H^{\ddagger} = 29.0 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = 1.1 \pm 2.4$ eu. The relatively small absolute value for the entropy of activation indicates an intramolecular mechanism for the reaction.

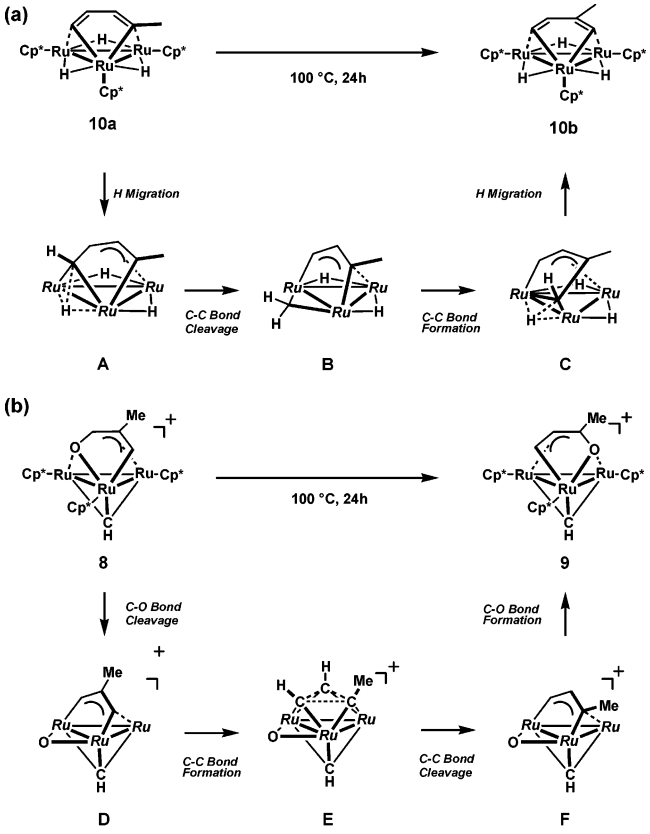
Previously, we reported a similar type of isomerization of the *nido*-ruthenacyclopentadiene complex **10a**. Upon heating, complex **10a** undergoes isomerization to be converted to **10b**, which is a positional isomer of the methyl group of the five-membered ruthenacycle (Scheme 5a). The activation parameters for this isomerization were estimated at $\Delta H^{\ddagger} = 26.2 \pm 2.2$ kcal/mol and $\Delta S^{\ddagger} = 8.6 \pm 0.4$ eu based on the kinetic study by means of ^{1}H NMR spectroscopy.[17] Notably, the activation parameters for the isomerization from **8** to **9** are comparable to those for the isomerization of the *nido*-ruthenacyclopentadiene complex **10a** to **10b**.

On the basis of the DFT calculation, we proposed a sequence of reactions for the mechanism of the isomerization from **10a** to **10b**, which involved a hydride transfer, C−C bond cleavage, and C−C bond re-formation. In the first step, the hydrido ligand located below the α-carbon atom of the ruthenacyclopentadiene moiety interacts with the α-carbon atom and forms an intermediate **A**, which possesses an agostic Ru−H−C interaction. Then, the C−C bond in the ruthenacyclic allyl species **A** was cleaved to form μ-methylene-μ_3-diruthenaallyl intermediate **B**. The isomerization process was completed by the reductive C−C coupling at another ruthenium center to form **C** followed by the H migration.[17]

There is a close structural analogy between the oxaruthenacycle complex **8** and the ruthenacyclic allyl intermediate **A**. On the basis of the mechanism shown in Scheme 5a, it is plausible that a μ-oxo-μ_3-2-methyldiruthenaallyl intermediate **D** is formed by the C−O bond cleavage (Scheme 5b). The intermediates **D** and **F** correspond to the μ-methylene-μ_3-diruthenaallyl intermediate **B**. But, additional rearrangement of the allylic moiety would be required for the methyl migration from the 4- to the 3-position of the oxaruthenacycle. Re-formation of the μ_3-η^3-C_3 ring leading to an intermediate **E** and subsequent C−C bond cleavage at the C(Me)−C(H) position yielding 1-methyldiruthenaallyl intermediate **F** should take place. Successive C−O bond formation at the quaternary carbon would furnish the skeletal rearrangement from **8** to **9**.

The key step for the migration of the methyl group would be re-formation of the μ_3-η^3-C_3 ring on the triruthenium core. We have shown that the highly charged metal center renders the skeletal rearrangement of the diruthenaallyl to the μ_3-η^3-C_3 ring structure as shown in Scheme 2.[10] Although complex **8** was monocationic, electron density of the metal center would substantially decrease due to the formation of a μ-oxo ligand.

Scheme 5



(17) Inagaki, A.; Musaev, D. G.; Takemori, T.; Suzuki, H.; Morokuma, K. *Organometallics* **2003**, *22*, 1718−1727.

Table 4. Crystallographic Data for 6-BF_4, 8-BPh_4, and 9-PF_6

	6-BF_4	8-BPh_4	9-PF_6
	(a) Crystal Data		
empirical formula	$C_{35}H_{58}B_2F_8O_4Ru_3$	$C_{59}H_{71}BORu_3$	$C_{35}H_{51}F_6OPRu_3$
fw	1019.64	1110.18	935.94
cryst description	prism	block	platelet
cryst color	red	green	green
cryst size	0.50 × 0.20 × 0.10 mm	0.80 × 0.80 × 0.50 mm	0.25 × 0.25 × 0.05 mm
crystallizing solution	THF (−30 °C)	acetone/water (−4 °C)	MeOH/THF (4 °C)
cryst syst	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$ (#2)	*Pbca* (#61)	$P\bar{1}$ (#2)
lattice params	a = 11.5978(9) Å	a = 19.5902(2) Å	a = 11.2603(6) Å
	b = 12.3053(9) Å	b = 19.8383(2) Å	b = 13.3116(7) Å
	c = 16.1981(15) Å	c = 26.3502(3) Å	c = 14.2274(6) Å
	α = 105.579(3)°		α = 92.738(3)°
	β = 92.274(5)°		β = 102.493(2)°
	γ = 98.537(4)°		γ = 102.0860(17)°
V	2194.4(3) Å^3	10240.64(19) Å^3	2026.24(17) Å^3
Z value	2	8	2
D_{calc}	1.543 g/cm^3	1.440 g/cm^3	1.534 g/cm^3
measurement temp	−110 °C	−50 °C	−20 °C
μ(Mo Kα)	1.086 mm^{-1}	0.913 mm^{-1}	1.195 mm^{-1}
	(b) Intensity Measurements		
diffractometer	RAXIS-RAPID	RAXIS-RAPID	RAXIS-RAPID
radiation	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite
$2\theta_{max}$	60°	55°	60°
no. of reflns collected	22 998	93 739	17 784
no. of indep reflns	11 935 (R_{int} = 0.0432)	12 711(R_{int} = 0.0351)	11 233 (R_{int} = 0.0255)
no. of reflns obsd ($>2\sigma$)	9740	9581	9747
abs corr type	numerical	numerical	empirical
abs transmn	0.9852 (min.),	0.6701 (min.),	0.7544 (min.),
	0.9958 (max.)	0.7573 (max.)	0.9427 (max.)
	(c) Refinement (SHELXL-97)		
R_1 ($I > 2\sigma(I)$)	0.0769	0.0208	0.0531
wR_2 ($I > 2\sigma(I)$)	0.2052	0.0456	0.1462
R_1 (all data)	0.0942	0.0305	0.0611
wR_2 (all data)	0.2183	0.0470	0.1531
no. of data/restraints/params	11 910/0/498	11 726/0/606	11 233/0/444
GOF	1.098	0.930	1.101
largest diff peak and hole	4.289 and −1.505 e·Å^{-3}	0.362 and −0.465 e·Å^{-3}	2.415 and −1.172 e·Å^{-3}

Conclusion

We have demonstrated introduction of an oxygen atom into the hydrocarbyl ligand on the triruthenium cluster by the reaction with water. The dicationic nature of **4** would play a key role in nucleophilic addition of water to the metal center as well as formation of the μ-hydroxo group. While neutral dimetalloallyl complexes of group 8 were shown to be thermally stable, the dicationic diruthenaallyl complex **6**, having a μ-hydroxo group, underwent C−O bond formation upon deprotonation, and μ_3-2-oxaruthenacyclopentenyl complex **8** was obtained. These results indicate the usefulness of an electron-deficient cluster for carbon−heteroatom bond formation.

The X-ray diffraction study suggests that the order of the formed C−O bond is between single and double. Therefore, the oxacycle of **8** can be regarded as a coordinated methacrolein. However, we could not obtain "free" methacrolein from **8** due to lack of reactivity toward dihydrogen. Protonation of **8** immediately regenerated a dicationic μ-hydroxo complex **6** as a result of C−O bond cleavage. Furthermore, thermolysis of **8** led to the formation of isomeric oxaruthenacycle complex **9** as a result of migration of the methyl group from the 4- to the 3-position of the oxaruthenacycle. On the basis of the mechanism proposed for the isomerization of the *nido*-ruthenacyclopentadiene complex **10a**, a mechanism for the skeletal rearrangement involving cleavage of the C−O bond leading to formation of a μ-oxo intermediate was proposed. Although the mechanism still remains unclear, isomerization from **8** to **9** would be caused by the reduction of the steric repulsion between the Cp* group and the methyl group on the oxacycle.

Currently, introduction of the functional group into other types of hydrocarbyl ligands on the Ru_3 plane and isolation of the functionalized ligand as an organic molecule are under investigation.

Experimental Section

General Procedures. All experiments were carried out under an argon atmosphere. All compounds were treated with Schlenk techniques. Dehydrated tetrahydrofuran, dichloromethane, and methanol used in this study were purchased from Kanto Chemicals and stored under an argon atmosphere. Acetone and acetone-d_6 were dried over MS-4A and stored under an argon atmosphere. Dichloromethane-d_2 was degassed and stored under an argon atmosphere. Deionized water was degassed and stored under an argon atmosphere. The dicationic mixture of **4a** and **4b** was prepared according to a previously published method in ref 10, namely, treatment of μ_3-methylidyne-μ_3-η^3-2-methyldiruthenaallyl complex (Cp*Ru)$_3$-(μ_3-CH)(μ_3-η^3-CHCMeCH)(μ-H) (**3**)[9] with 2 equiv of ferrocenium salt. IR spectra were recorded on a Nicolet AVATAR 360 E.S.P. spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer with tetramethylsilane as an internal standard. Elemental analyses were performed on a Perkin-Elmer 2400II.

X-ray Structure Determination. X-ray-quality crystals of **6-BF_4**, **8-BPh_4**, and **9-PF_6** were obtained from the preparations described below and mounted on glass fibers. Diffraction experi-

ments of **6-BF$_4$**, **8-BPh$_4$**, and **9-PF$_6$** were performed on a Rigaku RAXIS-RAPID imaging plate with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at −110, −50, and −20 °C, respectively. The structures of **6**, **8**, and **9** were solved by a Patterson method and subsequent Fourier difference techniques. The structures were refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculation on F^2 using the SHELX-97 program package. All hydrogen atoms except for that of the bridging hydroxo group of **6**, which was not located during sequential difference Fourier synthesis, were refined isotropically. Neutral atom scattering factors were obtained from the standard sources.[18] Crystal data and results of the analyses are listed in Table 4.

Preparation of the Hexafluorophosphate Salt of [(Cp*Ru)$_3$-(μ-OH)(μ_3-CH)-(μ_3-η^1:η^3:η^1-CHCMeCH)]$^{2+}$ (6). Acetone (5 mL) and an equilibrated mixture of hexafluorophosphate salts of the dicationic μ_3-η^3-C$_3$ complexes [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^3-C$_3$MeH$_2$)-(μ-H)]$^{2+}$ (**4a** and **4b**, 34.2 mg, 0.0321 mmol) were charged in a reaction flask. After water (1 mL) was added to the solution, the solution was vigorously stirred for 60 h at 50 °C. The color of the solution changed from brown to purple. After the solvent was removed under reduced pressure, the residual solid was washed with 5 mL of THF three times to remove the monocationic μ_3-η^3-C$_3$ complex [(Cp*Ru)$_3$(μ_3-CH)(μ_3-η^3-C$_3$MeH$_2$)]$^+$ (**5**). On the basis of the ^{1}H NMR spectra of the obtained mixture, the ratio between **5** and **6** was estimated to be 35:65. A 7.1 mg amount of the hexafluorophosphate salt of **6** was obtained as a purple solid on drying under reduced pressure (20% yield). A single crystal used for the diffraction studies was prepared from the THF solution of **6** in the presence of HBF$_4$·OMe$_2$ stored at −30 °C. ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ 1.93 (s, 15H, C$_5$*Me*$_5$), 1.97 (s, 30H, C$_5$*Me*$_5$), 2.49 (s, 3H, μ_3-η^3-CHC*Me*CH), 8.58 (s, 1H, μ-O*H*), 10.09 (s, 2H, μ_3-η^3-C*H*CMeC*H*), 15.05 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 23 °C, acetone-d_6): δ 10.3 (q, J_{CH} = 128.7 Hz, C$_5$*Me*$_5$), 10.7 (q, J_{CH} = 126.7 Hz, C$_5$*Me*$_5$), 20.2 (q, J_{CH} = 128.8 Hz, μ_3-η^3-CHC*Me*CH), 103.3 (s, *C*$_5$Me$_5$), 105.5 (s, *C*$_5$Me$_5$), 108.1 (s, μ_3-η^3-CH*C*MeCH), 194.1 (d, J_{CH} = 162.1 Hz, μ_3-η^3-*C*HCMe*C*H), 324.9 (d, J_{CH} = 173.0 Hz, μ_3-*C*H). IR (ATR): 804, 836, 1021, 1091, 1261, 1380, 1430, 1463, 2919, 2962 (cm^{-1}). Anal. Calcd for C$_{35}$H$_{52}$B$_2$F$_8$ORu$_3$·3H$_2$O: C, 41.23; H, 5.73. Found: C, 41.52; H, 5.49.

Preparation of the Hexafluorophosphate salt of [(Cp*Ru)$_3$-(μ_3-CH){μ_3-OC(H)C(Me)CH−}]$^+$ (8). Dichloromethane (5 mL) and a hexafluorophosphate salt of [(Cp*Ru)$_3$(μ-OH)(μ_3-CH)(μ_3-η^1:η^3:η^1-CHCMeCH)]$^{2+}$ (**6**) (74.0 mg, 0.0776 mmol) were charged in a reaction flask. After triethylamine (35 μL, 0.249 mmol) was added to the solution at room temperature, the solution was vigorously stirred for 2 h. The color of the solution changed from purple to green. After the solvent was removed under reduced pressure, the residual solid was dissolved in 2 mL of THF. The residual solid was then purified by the use of column chromatography on alumina (Merck, Art. No. 1097) with tetrahydrofuran/methanol (1:1). Removal of the solvent under reduced pressure afforded the hexafluorophosphate salt of **8** (34.5 mg, 0.0369 mmol) as a dark green solid (48% yield). X-ray diffraction studies were carried out on a tetraphenylborate salt of **8**, which was obtained by adding a large excess amount of NaBPh$_4$ to a methanol solution of **8**. A single crystal used for the diffraction studies was prepared from an acetone/H$_2$O solution of **8-BPh$_4$** stored at −4 °C. ^{1}H NMR (400 MHz, 23 °C, CD$_2$Cl$_2$): δ 1.58 (s, 15H, C$_5$*Me*$_5$), 1.73 (s, 15H, C$_5$*Me*$_5$), 1.84 (s, 15H, C$_5$*Me*$_5$), 2.18 (s, 3H, μ_3-OC(H)C(*Me*)C(H)−), 5.87 (d, J_{HH} = 2.0 Hz, 1H, μ_3-OC(*H*)C(Me)C(H)−), 8.58 (d, J_{HH} = 2.0 Hz, 1H, μ_3-OC(H)C(Me)C(*H*)−), 16.84 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 23 °C, CD$_2$Cl$_2$): δ 9.9 (q, J_{CH} = 128.7 Hz, C$_5$*Me*$_5$), 10.4 (q, J_{CH} = 128.7 Hz, C$_5$*Me*$_5$), 10.7 (q, J_{CH} = 126.1 Hz, C$_5$*Me*$_5$), 16.8 (q, J_{CH} = 127.1 Hz, μ_3-OC(H)C(*Me*)C(H)−), 71.3 (s, μ_3-OC(H)*C*(Me)C(H)−), 84.3 (d, J_{CH} = 180.7 Hz, μ_3-O*C*(H)C(Me)C(H)−), 95.7 (s, *C*$_5$Me$_5$), 96.1 (s, *C*$_5$Me$_5$), 97.5 (s, *C*$_5$Me$_5$), 176.2 (d, J_{CH} = 164.9 Hz, μ_3-OC(H)C(Me)*C*(H)−), 336.5 (d, J_{CH} = 169.9 Hz, μ_3-*C*H). HMQC: δ_H 5.87−δ_C 84.3, δ_H 8.25−δ_C 176.2. IR (ATR): 704, 732, 864, 903, 927, 1021, 1072, 1261, 1374, 1425, 1447, 1481, 2913, 2983, 3029, 3054 (cm^{-1}). Anal. Calcd for C$_{35}$H$_{51}$F$_6$OPRu$_3$: C, 44.91; H, 5.49. Found: C, 44.52; H, 5.49.

Protonation of [(Cp*Ru)$_3$(μ_3-CH){μ_3-OC(H)C(Me)CH−}]$^+$ (8). Dichloromethane-d_2 (0.4 mL) and the hexafluorophosphate salt of **8** (11.2 mg, 0.012 mmol) were charged in an NMR tube with cyclooctane (2 μL, 0.015 mmol) as an internal standard. A large excess amount of trifluoroacetic acid (10 μL, 0.130 mmol) was then added to the NMR tube. The solution was allowed to react for 0.5 h. Quantitative formation of the dicationic μ-hydroxo complex **6** was confirmed by the ^{1}H NMR spectrum. Addition of D$_2$O to the solution resulted in the disappearance of the signal at δ 6.79 in the ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, 23 °C, CD$_2$Cl$_2$): δ 1.78 (s, 15H, C$_5$*Me*$_5$), 1.84 (s, 30H, C$_5$*Me*$_5$), 2.45 (s, 3H, μ_3-η^3-CHC*Me*CH), 6.79 (s, 1H, μ-O*H*), 9.63 (s, 2H, μ_3-η^3-C*H*CMeC*H*), 14.29 (s, 1H, μ_3-C*H*). A broad signal derived from the remaining CF$_3$COOH was also observed at δ 10.1. ^{13}C NMR (400 MHz, 23 °C, CD$_2$Cl$_2$): δ 9.9 (q, J_{C-H} = 128.2 Hz, C$_5$*Me*$_5$), 10.4 (q, J_{C-H} = 128.2 Hz, C$_5$*Me*$_5$), 20.2 (q, J_{C-H} = 128.2 Hz, μ_3-η^3-CHC*Me*CH), 103.1 (s, *C*$_5$Me$_5$), 105.5 (s, *C*$_5$Me$_5$), 108.4 (s, μ_3-η^3-CH*C*MeCH), 193.8 (d, J_{C-H} = 160.9 Hz, μ_3-η^3-*C*HCMe*C*H), 324.3 (d, J_{C-H} = 174.0 Hz, μ_3-*C*H).

Preparation of a Hexafluorophosphate Salt of [(Cp*Ru)$_3$(μ_3-CH){μ_3-OC(Me)C(H)C(H)−}]$^+$ (9). THF (10 mL) and the hexafluorophosphate salt of [(Cp*Ru)$_3$(μ_3-CH){μ_3-OC(H)C(Me)-CH−}]$^+$ (**8**) (34.5 mg, 0.0369 mmol) were charged in a glass autoclave. The solution was heated at 100 °C for 24 h. Removal of the solvent under reduced pressure afforded the hexafluorophosphate salt of **9** (30.5 mg, 0.0326 mmol) as a green solid (88% yield). A single crystal used for the diffraction studies was prepared from a THF solution of **9** stored at −30 °C. ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ 1.66 (s, 15H, C$_5$*Me*$_5$), 1.83 (s, 15H, C$_5$*Me*$_5$), 1.91 (s, 15H, C$_5$*Me*$_5$), 2.16 (s, 3H, μ_3-OC(*Me*)C(H)C(H)−), 4.20 (d, J_{HH} = 4.4 Hz, 1H, μ_3-OC(Me)C(*H*)C(H)−), 8.35 (d, J_{HH} = 4.4 Hz, 1H, 1H, μ_3-OC(Me)C(H)C(*H*)−), 17.14 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 23 °C, acetone-d_6): 10.8 (q, J_{CH} = 127.0 Hz, C$_5$*Me*$_5$), 10.9 (q, J_{CH} = 127.0 Hz, C$_5$*Me*$_5$), 11.5 (q, J_{CH} = 126.6 Hz, C$_5$Me$_5$), 25.9 (q, J_{CH} = 127.8 Hz, μ_3-OC(*Me*)C(H)C(H)−), 71.3 (d, J_{CH} = 164.2 Hz, μ_3-OC(Me)*C*(H)C(H)−), 95.7 (s, *C*$_5$Me$_5$), 96.8 (s, *C*$_5$Me$_5$), 98.3 (s, *C*$_5$Me$_5$), 109.5 (s, μ_3-O*C*(Me)C(H)C(H)−), 174.9 (d, J_{CH} = 168.4 Hz, μ_3-OC(Me)C(H)*C*(H)−), 339.9 (d, J_{CH} = 161.1 Hz, μ_3-*C*H). HMQC: δ_H 4.20−δ_C 71.2, δ_H 8.35−δ_C 174.9. IR (ATR): 836, 874, 911, 1020, 1072, 1262, 1287, 1377, 1457, 2912, 2961 (cm^{-1}). Anal. Calcd for C$_{35}$H$_{51}$F$_6$OPRu$_3$: C, 44.91; H, 5.49. Found: C, 45.14; H, 5.65.

Kinetic Experiments of the Isomerization of 8 to 9. The hexafluorophosphate salt of **8** (18.2 mg, 0.019 mmol) was dissolved in DMSO-d_6 (2.0 mL), and the solution was divided into four equal parts and charged in NMR tubes, respectively. After the NMR tube was sealed, the solution was allowed to react. The reaction proceeded at 60, 90, 100, and 110 °C. The consumption of **8** was monitored at each temperature by means of ^{1}H NMR spectroscopy, and the intensities of the resonances at δ 5.87 and 8.58, which were assignable to the methine protons of the oxacycle moiety, were recorded periodically. At regular times, the distribution of **8** was estimated by dividing the integral value for **8** by the sum of the integral values for **8** and **9**. This value was used for the determination of the rate constant. Temperature dependence of the rate constant was used in deriving activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The rate constants obtained at each temperature were as follows: k_{333K} = 1.08 × 10^{-6} s^{-1}, k_{363K} = 5.39 × 10^{-5} s^{-1}, k_{373K} = 1.33 × 10^{-4} s^{-1}, and k_{383K} = 3.70 × 10^{-4} s^{-1}.

(18) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.

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Supporting Information Available: Results of the X-ray diffraction studies and crystallographic files of **6-BF_4**, **8-BPh_4**, and **9-PF_6**. The X-ray data are also given as CIF files. Results of kinetic study on the deprotonation of the dicationic mixture of **7a** and **7b** in acetone/methanol are also given. These materials are available free of charge via the Internet at http://pubs.acs.org

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