Articles

Insertion of Acetylene and Nitriles into a Ru−C Bond of a Dicationic Triruthenium Complex Having a μ_3-η^3-C_3 Ring: Formation of Six-Membered Ruthenacycles on a Triruthenium Core

Toshiro Takao, Makoto Moriya, and Hiroharu Suzuki*

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

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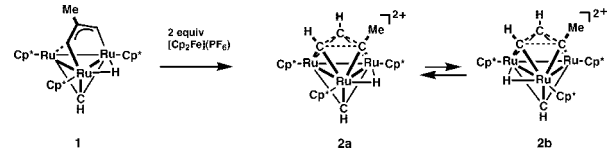
A triruthenium complex having a μ_3-ruthenacyclohexadienyl moiety, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-}CHCMe{=}CH{-}CH{=}CH{-})\}(\mu_3\text{-}CH)]^+$ (**9**), was synthesized by the reaction of an equilibrating mixture of dicationic complexes having a μ_3-η^3-C_3 ring, $[(Cp^*Ru)_3(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)(\mu_3\text{-}CH)(\mu\text{-}H)]^{2+}$ (**2a** and **2b**), with acetylene. The protonation of **9** resulting in the formation of a dicationic μ_3-ruthenacyclohexadienyl complex, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-}CH{-}CMe{=}CHCH{=}CH{-})\}(\mu_3\text{-}CH)(\mu\text{-}H)]^{2+}$ (**10**), strongly indicates that the hydrido ligand of **2** was removed as a proton after the six-membered metallacycle was formed by the insertion of an acetylene molecule into a Ru−C bond. The thermolysis of **9** resulted in an isomerization of the metallacycle moiety via the formation of a μ_3-cyclopentadienyl intermediate and quantitatively afforded a μ_3-4-methylruthenacyclohexadienyl complex, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^3\text{:}\eta^2\text{-}CHCHCMe{-}CH{=}CH{-})\}(\mu_3\text{-}CH)]^+$ (**13**). Nitriles also inserted into a Ru−C bond of **2** and afforded a series of dicationic 2-azaruthenacyclohexadienyl complexes, $[(Cp^*Ru)_2\{Cp^*Ru\ (\mu_3\text{-}\eta^2\text{:}\eta^3\text{-}NH{=}CR{-}CHCMeCH{-})\}(\mu_3\text{-}CH)]^{2+}$ (**18a**: R = Me, **18b**: R = Et, **18c**: R = Ph).

Introduction

Recently, we showed that the μ_3-diruthenaallyl complex $(Cp^*Ru)_3(\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-}CHCMeCH)(\mu_3\text{-}CH)(\mu\text{-}H)$ (**1**)[1] was converted to an equilibrium mixture of dicationic triruthenium complexes having a μ_3-η^3-C_3 ring, $[(Cp^*Ru)_3(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)(\mu_3\text{-}CH)(\mu\text{-}H)]^{2+}$ (**2a** and **2b**), via the reductive C−C bond formation between the two terminal carbon atoms of the diruthenaallyl ligand upon chemical oxidation (eq 1).[2] While complex **1** was robust and inert toward air and moisture, the dicationic complex **2** reacts with H_2O, CO, and $CHCl_3$ (Scheme 1).[2,3] As seen in the formation of the oxaruthenacycle complex **8**, the electron deficiency at the allylic carbon atom of **2** induces the attack of nucleophiles.

As shown in Scheme 1, the regioselective cleavage of the C(H)−C(H) bond of the μ_3-η^3-C_3 ring of **2a**,**b** occurred in the reactions with $CHCl_3$, CO, and water. Such a regioselectivity in the reaction of **2** is explicable in terms of the equilibrium between **2a**,**b** and **3**, although **3** is not detected by means of ^{1}H NMR spectroscopy.

The C−C bond forming reaction on a cluster core is relevant to many catalytic reactions performed on a metal surface, and the reaction chemistry of the cluster complex has provided important mechanistic insights in this area.[4] While many studies have been carried out in relation to the C−C bond formation,[5] significantly limited efforts have been devoted to the reactivity of the μ_3-η^3-dimetalloallyl complexes in comparison to their syntheses.[6,7]



(1)

In the course of our research on the reactivity of the mixture of **2a** and **2b**, we examined the reaction of **2** with acetylene and nitriles. In this article, we report the unprecedented reaction of complexes **2a**,**b** resulting in the formation of six-membered ruthenacycles by the insertion of acetylene or nitrile into a Ru−C bond. The skeletal rearrangement of the cationic μ_3-ruthenacyclohexadienyl complex **9** leading to the positional isomer **13** via a μ_3-cyclopentadienyl intermediate is also mentioned.

Result and Discussion

The treatment of **2a**,**b** with 1 atm of acetylene at ambient temperature resulted in the quantitative formation of a mono-

(1) Inagaki, A.; Takao, T.; Moriya, M.; Suzuki, H. *Organometallics* **2003**, *22*, 2196–2198.
(2) Takao, T.; Moriya, M.; Suzuki, H. *Organometallics* **2007**, *26*, 1349–1360.
(3) Moriya, M.; Takao, T.; Suzuki, H. *Organometallics* **2007**, *26*, 1650–1657.
(4) (a) Knox, S. A. R. *J. Cluster. Sci.* **1992**, *3*, 385–396. (b) Jeffery, J. C.; Went, M. J. *Polyhedron* **1988**, *7*, 775–790.
(5) (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203–239. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219–284. (c) Sappa, E. *J. Cluster Sci.* **1994**, *5*, 211–263. (d) Deabate, S.; Giordano, R.; Sappa, E. *J. Cluster Sci.* **1997**, *8*, 407–457.

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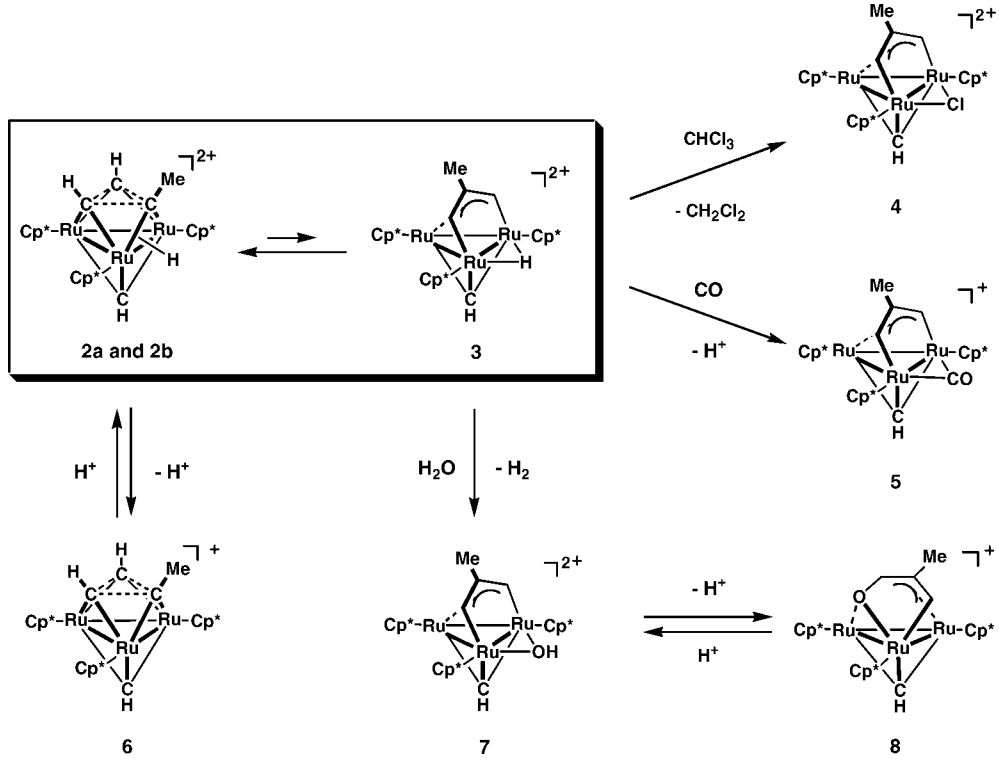
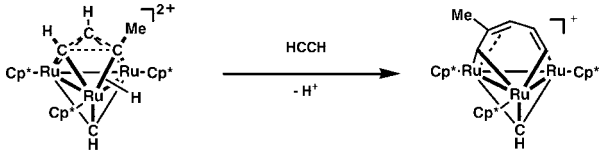
Scheme 1. Reactivity of 2a,b



cationic μ_3-3-methylruthenacyclohexadienyl complex, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-}CH-CMe=CH-CH=CH-)\}(\mu_3\text{-}CH)]^+$ (**9**), via the insertion of acetylene into a Ru−C bond (eq 2). Acetylene most probably reacted with the μ_3-diruthenaallyl intermediate **3**, which was equilibrated with **2a** and **2b**. A hydrido ligand of **2** was eliminated as hexafluorophosphoric acid during the reaction, and the charge of the complex was reduced to +1.



(2)

A red, single crystal of the hexafluorophosphate salt of **9**, which was suitable for the diffraction study, was obtained from cold MeOH solution. The molecular structure of **9** is shown in Figure 1, and the relevant bond lengths and angles are listed in Table 1. The diffraction study indicated the formation of a six-membered metallacycle on the triruthenium core.

Several dinuclear complexes containing a bridging six-membered metallacycle (η^6-metallabenzene) are known.[8] To the best of our knowledge, this is the first example of the metallacyclohexadienyl ligand formed on a trimetallic plane.[9] Unlike the six-membered metallacycle of the dinuclear complexes in which the five carbon atoms are almost coplanar, the six-membered ring of **9** is folded and adopts a boat conformation. As shown in Figure 1, the four carbon atoms, C(2), C(3), C(5), and C(6), are almost coplanar, and the torsion angles, Ru(1)−C(2)−C(6)−C(5) and C(4)−C(5)−C(3)−C(2) are 149.4° and 142.6°, respectively.

The Ru(1)−C(2) and Ru(1)−C(6) distances are 2.073 (3) and 1.977 (3) Å, respectively, and almost correspond to those of the Ru−C(1) single bonds (1.917(3)−2.042(3) Å). On the basis of the folded structure, the six-membered ring of **9** is most likely envisaged as a ruthenacyclohexadienyl rather than a ruthenabenzene complex.

The C(5)−C(6) moiety, which stems from the added acetylene, is σ-bonded to Ru(1) and π-bonded to Ru(3). The C(2), C(3), and C(4) atoms are derived from the μ_3-η^3-C$_3$

(6) (a) Bruce, M. I.; Cairns, M. A.; Cox, A.; Green, M.; Smith, M. D. H.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1970**, 735–736. (b) Parkins, A. W.; Fischer, E. O.; Huttner, G.; Regler, D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 633. (c) Gambino, O.; Valle, M.; Aime, S.; Vaglio, G. A. *Inorg. Chim. Acta* **1974**, *8*, 71–75. (d) Castiglioni, M.; Milone, L.; Osella, D.; Vaglio, G. A.; Valle, M. *Inorg. Chem.* **1976**, *15*, 394–396. (e) Aime, S.; Tiripicchio, A.; Camellini, M.; Deeming, A. J. *Inorg. Chem.* **1981**, *20*, 2027–2031. (f) Clauss, A. D.; Shapley, J. R.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 7387–7388. (g) Beanan, L. R.; Rahman, Z. A.; Keister, J. B. *Organometallics* **1983**, *2*, 1062–1064. (h) Aime, S.; Osella, D.; Deeming, A. J.; Arce, A. J.; Hursthouse, M. B.; Dawes, H. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1459–1463. (i) Nuel, D.; Mathieu, R. *Organometallics* **1988**, *7*, 16–21. (j) Adams, R. D.; Babin, J. E.; Tasi, M.; Wang, J.-G. *Organometallics* **1988**, *7*, 755–764. (k) Churchill, M. R.; Ziller, J. W.; Shapley, J. R.; Teh, W.-Y. *J. Organomet. Chem.* **1988**, *353*, 103–117. (l) Lentz, D.; Michael, H. *Chem. Ber.* **1988**, *121*, 1413–1416. (m) Ziller, J. W.; Bower, D. K.; Dalton, D. M.; Keister, J. B.; Churchill, M. R. *Organometallics* **1989**, *8*, 492–497. (n) Chen, H.; Johnson, B. F. G.; Lewis, J.; Braga, D.; Grepioni, F. *J. Organomet. Chem.* **1990**, *398*, 159–164. (o) Park, J. T.; Woo, B. W.; Chung, J.-H.; Shim, S. C.; Lee, J.-H.; Lim, S.-S.; Suh, I.-H. *Organometallics* **1994**, *13*, 3384–3386. (p) Wong, W.-Y.; Chan, S.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1995**, 1497–1509. (q) Blake, A. J.; Dyson, P. J.; Gaede, P. E.; Johnson, B. F. G.; Parsons, S. *Organometallics* **1996**, *15*, 4100–4103. (r) Adams, K. J.; Barker, J. J.; Knox, S. A. R.; Orpen, A. G. *Dalton* **1996**, 975–988. (s) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *Dalton* **1999**, 2777–2783. (t) Cabeza, J. A.; Silva, I.; Río, I.; García-Granda, S.; Riera, V. *Inorg. Chim. Acta* **2003**, *347*, 107–113.

(7) (a) Aime, S.; Milone, L.; Osella, D.; Valle, M. *J. Chem. Res. (M)* **1978**, 782–790. (b) Aime, S.; Milone, L.; Osella, D.; Valle, M. *J. Chem. Res. (S)* **1978**, 77. (c) Bruce, M. I.; Surynt, R. J.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1997**, *50*, 701–704. (d) Bruce, M. I.; Gulbis, J. M.; Humphrey, P. A.; Surynt, R. J.; Tiekink, E. R. T. *Aust. J. Chem.* **1997**, *50*, 875–878.

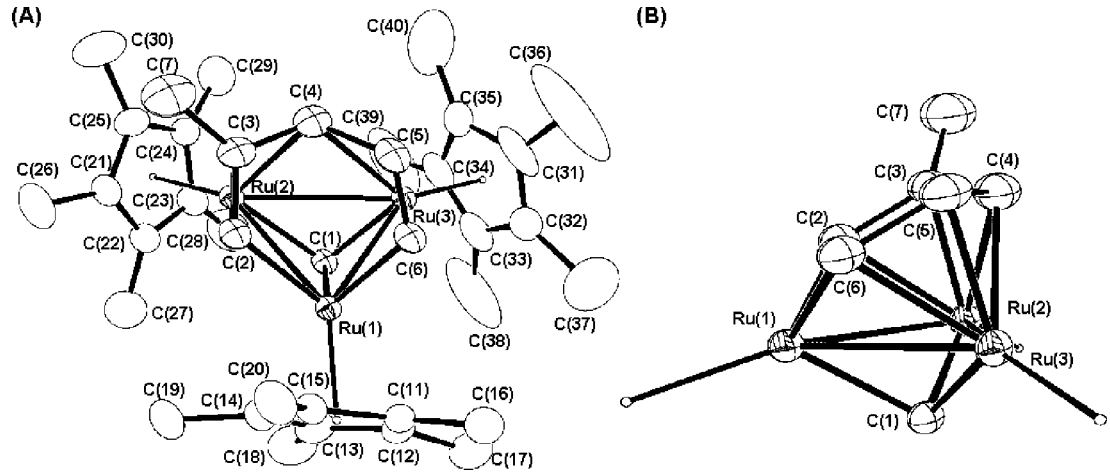


Figure 1. Molecular structure and labeling scheme of **9** with thermal ellipsoids at the 30% probability level. The anionic moiety (PF_6^-) is omitted for clarity. (b) Side view of the core of **9**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 9, 13, and 18c

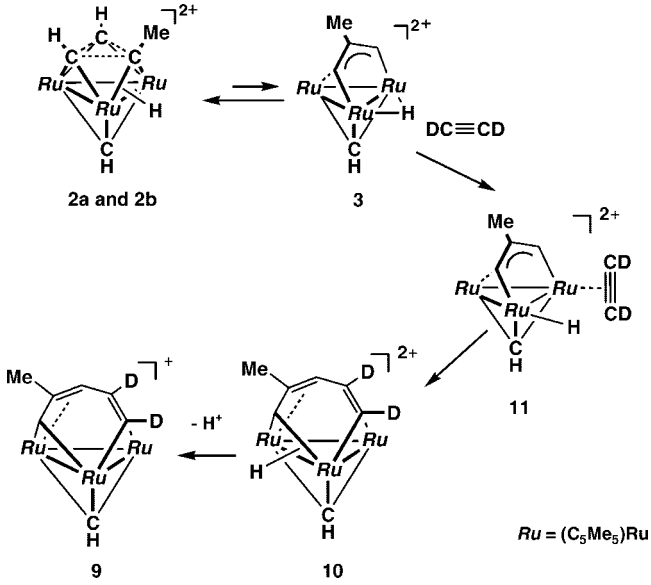
	9-PF_6		**13-BPh_4**		**18c-PF_6**
Ru(1)−Ru(2)	2.9155(4)		2.7300(3)		2.7414(4)
Ru(1)−Ru(3)	2.6322(3)		2.7181(3)		2.7258(4)
Ru(2)−Ru(3)	2.8251(3)		2.9249(3)		2.9616(4)
Ru(1)−C(1)	2.042(3)		2.033(2)		2.041(4)
Ru(2)−C(1)	2.038(3)		2.001(3)		2.006(4)
Ru(3)−C(1)	1.917(3)		1.988(2)		1.999(3)
Ru(1)−C(2)	2.073(4)		2.032(3)	Ru(1)−N(1)	2.050(3)
Ru(1)−C(6)	1.977(3)		2.027(3)		2.047(4)
C(2)−C(3)	1.440(5)		1.407(4)	N(1)−C(3)	1.372(4)
C(3)−C(4)	1.348(5)		1.407(4)		1.439(5)
C(4)−C(5)	1.470(6)		1.443(4)		1.458(6)
C(5)−C(6)	1.463(5)		1.407(4)		1.393(6)
Ru(2)−C(2)	2.147(4)		2.134(3)	Ru(2)−N(1)	2.104(3)
Ru(2)−C(3)	2.184(4)		2.169(3)		2.209(3)
Ru(2)−C(4)	2.509(4)		2.524(3)		2.598(4)
Ru(3)−C(4)	2.485(4)		2.704(3)		2.352(4)
Ru(3)−C(5)	2.131(4)		2.156(3)		2.184(3)
Ru(3)−C(6)	2.146(3)		2.109(3)		2.118(4)
C(3)−C(7)	1.534(5)	C(4)−C(7)	1.512(4)		1.484(5)
				C(5)−C(13)	1.523(5)
Ru(2)−Ru(1)−Ru(3)	60.973(9)		64.940(8)		65.599(11)
Ru(1)−Ru(2)−Ru(3)	54.556(8)		57.332(7)		56.947(10)
Ru(1)−Ru(3)−Ru(2)	64.472(9)		57.728(7)		57.455(10)
Ru(2)−Ru(1)−C(2)	47.35(10)		50.68(8)	Ru(2)−Ru(1)−N(1)	49.55(9)
Ru(3)−Ru(1)−C(6)	53.21(10)		50.22(8)		50.26(10)
C(2)−Ru(1)−C(6)	82.32(16)		85.23(12)	N(1)−Ru(1)−C(6)	86.04(14)
Ru(1)−C(2)−Ru(2)	87.39(13)		81.85(10)	Ru(1)−N(1)−Ru(2)	82.58(11)
Ru(1)−C(2)−C(3)	130.0(3)		124.5(2)	Ru(1)− N(1)−C(3)	125.4(2)
Ru(2)−C(2)−C(3)	72.0(2)		72.30(17)	Ru(2)− N(1)−C(3)	75.68(19)
Ru(2)−C(3)−C(2)	69.2(2)		69.55(16)	Ru(2)−C(3)−N(1)	67.33(18)
Ru(2)−C(3)−C(4)	87.2(3)		87.05(18)		88.2(2)
C(2)−C(3)−C(4)	116.0(3)		122.1(3)	N(1)−C(3)−C(4)	115.8(3)
C(3)−C(4)−C(5)	115.0(4)		118.7(3)		117.2(3)
Ru(3)−C(5)−C(4)	85.2(2)		95.37(17)		77.6(2)
Ru(3)−C(5)−C(6)	70.5(2)		68.92(16)		68.5(2)
C(4)−C(5)−C(6)	125.7(3)		122.7(3)		118.1(3)
Ru(1)−C(6)−Ru(3)	79.25(12)		82.15(9)		81.75(13)
Ru(1)−C(6)−C(5)	121.3(3)		122.9(2)		122.4(3)
Ru(3)−C(6)−C(5)	69.5(2)		72.56(16)		73.7(2)

ring of **2**. Unlike the diruthenaallyl structure, bond alternation was observed in the C_3 moiety. The differences in the bond distances between C(2)−C(3) and C(3)−C(4) (1.440(5) and 1.348 (5) Å, respectively) indicate that the C(2)−C(4) moiety is regarded as a σ-allyl group that is π-bonded to Ru(2).

The three Ru atoms form a scalene triangle with sides of 2.6322(3), 2.8251(3), and 2.9155(4) Å. Among the three Ru−Ru bonds, Ru(1)−Ru(2) is the longest (2.9155(4) Å). This is probably due to the steric repulsion between the methyl group at C(3) and the Cp* group bound to Ru(2) (*vide infra*).

In the ^{1}H NMR spectrum of **9**, signals due to the four methine protons appear at δ 8.08 (dd, J_{H-H} = 5.6, 2.0 Hz, C^6H), 7.94 (d, J_{H-H} = 2.4 Hz, C^2H), 4.09 (dd, J_{H-H} = 6.0, 5.6 Hz, C^5H), and 2.94 (ddd, J_{H-H} = 6.0, 2.4, 2.0 Hz, C^4H). The chemical shifts of δ 7.94 and 8.08 reflect the carbenic character of the C(2) and C(6) atoms.[10] Their carbenic character is also confirmed by the chemical shifts and J_{C-H} values of the ^{13}C

Scheme 2. Plausible Mechanism for the Formation of 9



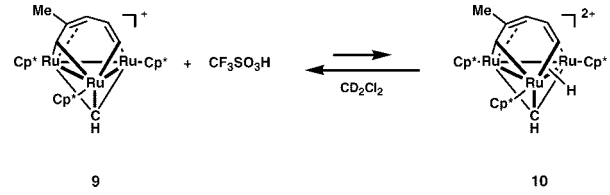
signals for C^2 and C^6 appearing at δ 177.3 (d, $J_{C-H} = 158$ Hz) and 179.0 (d, $J_{C-H} = 156$ Hz), respectively.[10]

The labeling experiment performed using deuterated acetylene confirmed the selective incorporation of the deuterium atoms into the C(5)−C(6) position of the ruthenacycle. The signals originated from the deuterated acetylene were observed at δ 7.99 and 3.94 in the ^{2}H NMR spectrum. The acetylene molecule inserted into a Ru−C bond probably via the formation of the π-bonded acetylene intermediate **11** shown in Scheme 2. The similar alkyne-μ_3-dimetalloallyl complex **12** was synthesized and structurally identified by Adams and co-workers.[11] The structural parameters of **12** indicated that the alkyne ligand acts as a 4*e*-donor. In contrast, the alkyne ligand of **11** should act as a 2*e*-donor according to the 18-electron rule.

While many five-membered metallacycles have been prepared by the coupling of two alkyne molecules on a metal center, the formation of a six-membered metallacycle via the insertion of an alkyne molecule into an M−C σ-bond is still rare; Girolami and co-workers synthesized an η^5-ruthenabenzene complex by the reaction of a diruthenium μ-methylene complex with two molecules of acetylene,[8g,j] and Bruce and co-workers synthesized two types of trimetallic complexes having a six-membered ruthenacycle by the reaction of a μ_3-allenylidene complex with terminal alkynes.[9b]

As mentioned above, the hydrido ligand of the dicationic complex **2** was liberated as a proton during the formation of **9**. The deprotonation should have occurred at least after the coordination of acetylene because the monocationic tris(μ-carbene) complex **6** did not react with acetylene. The protonation of **9** was thus examined in order to gain a direct insight into the reaction mechanism.

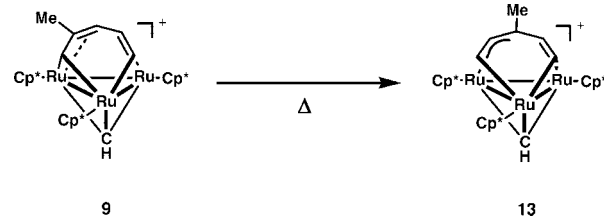
The reaction of **9** with a large excess amount of trifluoromethanesulfonic acid was carried out in CD_2Cl_2 solution, which resulted in the exclusive formation of a dicationic μ_3-ruthenacyclohexadienyl complex, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-}CH-CMe=H-CH=H-)\}(\mu_3\text{-}CH)(\mu\text{-}H)]^{2+}$ (**10**) (eq 3). The ^{1}H NMR spectrum of **10** revealed a signal due to the hydrido ligand generated in the reaction as a singlet at δ –18.95. Complex **10** was formed only in the presence of a large excess amount of CF_3SO_3H in solution; formation of **10** was not observed when CF_3COOH was used instead of CF_3SO_3H. Due to the inclined equilibrium between **9** and **10**, **10** was not isolated,unfortunately. Thus, the position of the hydrido ligand was not determined.



(3)

The methine signals of the ruthenacyclohexadienyl moiety of **10** appeared at δ 9.12 (d, $J_{H-H} = 2.4$ Hz, C^2H), 9.11 (dd, $J_{H-H} = 5.2$, 1.6 Hz, C^6H), 5.00 (ddd, $J_{H-H} = 5.6$, 2.4, 1.6 Hz, C^4H), and 4.06 (dd, $J_{H-H} = 5.6$, 5.6 Hz, C^5H). Although these signals appeared at slightly lower magnetic fields than those of the monocationic **9**, the coupling patterns among the former showed a significant resemblance to those of **9**. This observation strongly suggested that the μ_3-ruthenacyclohexadienyl skeleton was also retained in **10**.

Upon heating at 140 °C, complex **9** isomerized to μ_3-4-methylruthenacyclohexadienyl complex $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^3\text{:}\eta^2\text{-}CHCHCMe-CH=CH-)\}(\mu_3\text{-}CH)]^+$ (**13**) (eq 4). The methyl group at the 3-position migrated to the 4-position of the ruthenacyclohexadienyl moiety; this observation was unambiguously corroborated by X-ray diffraction studies. The molecular structure of **13** is shown in Figure 2, and the selected bond lengths and angles are listed in Table 1.



(4)

The six-membered ruthenacycle again adopts a boat conformation. While the methyl group of the ruthenacyclohexadienyl moiety of **9** is directed toward the Cp* group on Ru(2), that of **13** is directed toward the space between the two Cp* groups. The space-filling models of these μ_3-ruthenacyclohexadienyl complexes are shown in Figure 3. Whereas the shortest interatomic C···C distance between the Cp* groups and the

(8) (a) Hein, J.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2211–2218. (b) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612–2614. (c) Bleeke, J. R.; Xie, Y.-F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4703–4704. (d) Bosch, H. W.; Hund, H.-U.; Nletlispach, D.; Salzer, A. *Organometallics* **1992**, *11*, 2087–2098. (e) Kralik, M. S.; Stahl, L.; Arif, A. M.; Strouse, C. E.; Ernst, R. D. *Organometallics* **1992**, *11*, 3617–3621. (f) Bleek, J. R.; Bass, L. A.; Xie, Y.-F.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4213–4219. (g) Lin, W.; Wilson, S. R.; Girolami, G. S. *J. Chem. Soc., Chem. Commun.* **1993**, 284–285. (h) Bertling, U.; Englert, U.; Salzer, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1003–1004. (i) Kralik, M. S.; Rheingold, A. L.; Hutchinson, J. P.; Freeman, J. W.; Ernst, R. D. *Organometallics* **1996**, *15*, 551–561. (j) Lin, W.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1997**, *16*, 2356–2361.

(9) (a) To the best of our knowledge, there are three examples of a trimetallic complex having a bridging metallacyclohexadienyl ligand. However, their five carbon atoms π-bonded to only one metal center, namely, adopting an "edge-capping" coordination. This is different from the "face-capping" coordination found in **9**: Boroni, E.; Costa, M.; Predieri, G.; Sappa, E.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1992**, 2585–2590. (b) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 1678–1686.

(10) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159–263.

(11) Adams, R. D.; Belinski, J. A. *Organometallics* **1991**, *10*, 2114–2120.

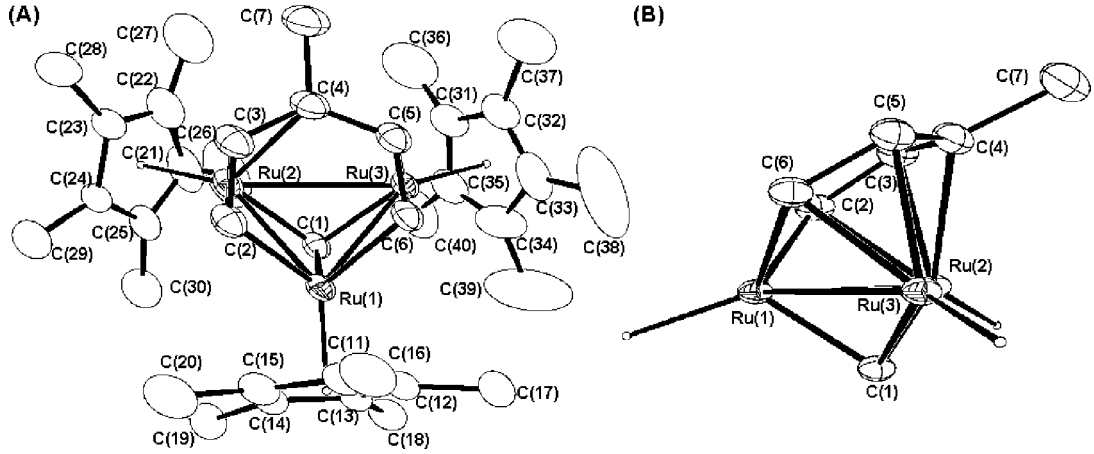


Figure 2. Molecular structure and labeling scheme of **13** with thermal ellipsoids at the 30% probability level. The anionic moiety (BPh_4^-) is omitted for clarity. (b) Side view of the core of **13**.

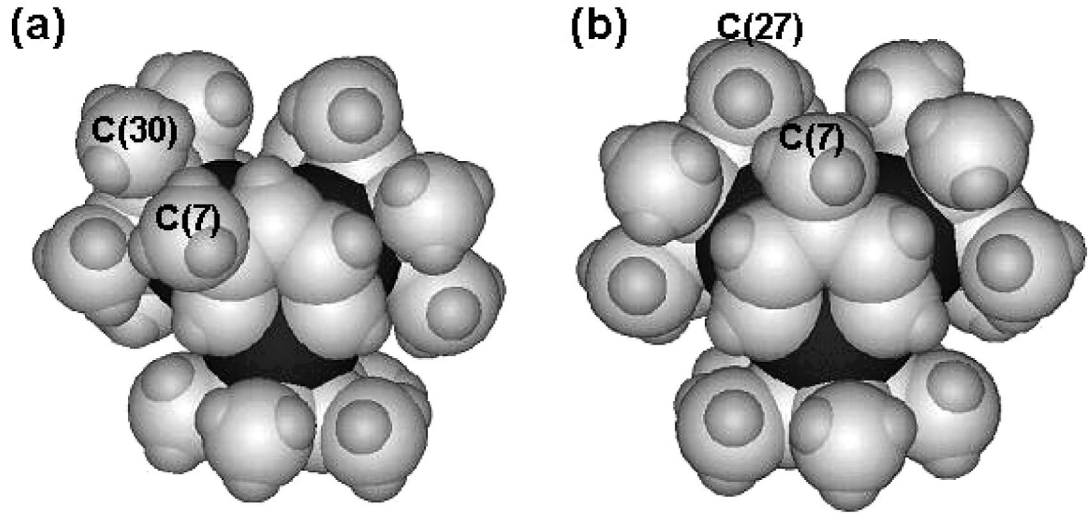
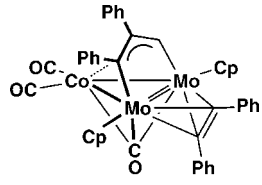


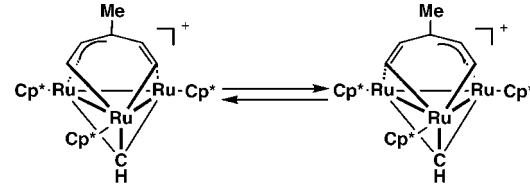
Figure 3. Space-filling models of the μ_3-ruthenacyclohexadienyl complexes: (a) **9** and (b) **13**. The anionic moieties are omitted for clarity.

Chart 1



12

Scheme 3. Tautomerization of 13



13 **13**

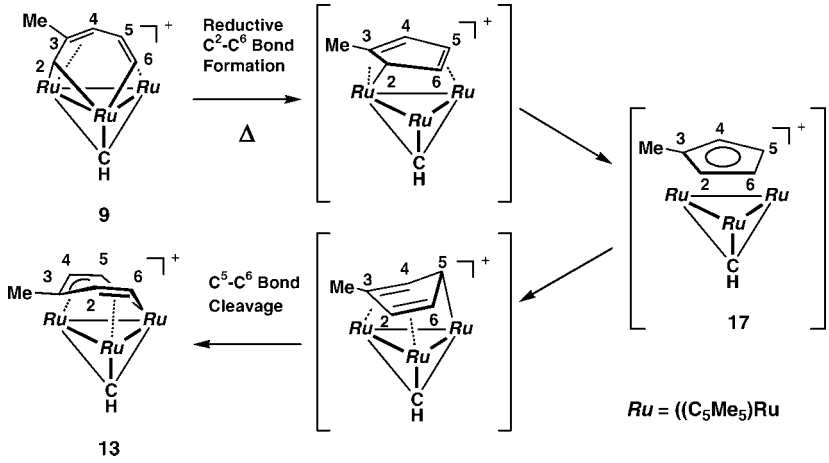
methyl group in the ruthenacycle of **9** is 3.372 Å (C(7)···C(30)), that becomes longer by ca. 0.3 Å in **13** (C(7)···C(27) = 3.679 Å). This suggests that the steric repulsion between the methyl group on the ruthenacyclohexadienyl moiety and the Cp* groups considerably decreases as a result of the isomerization. This is most likely the driving force of this skeletal rearrangement, which is consistent with the fact that the reaction from **9** to **13** was irreversible.

Probably due to the reduction of the steric repulsion, the Ru_3 core becomes an isosceles triangle with sides of 2.9249(3), 2.7300(3), and 2.7181(3) Å. In addition, bond alternation was no longer found among the C(2), C(3), and C(4) atoms (C(2)−C(3) = 1.407(4) Å and C(3)−C(4) = 1.407(4) Å), unlike the parent complex **9**. This shows that these atoms interact with the Ru(2) as a π-allyl ligand.

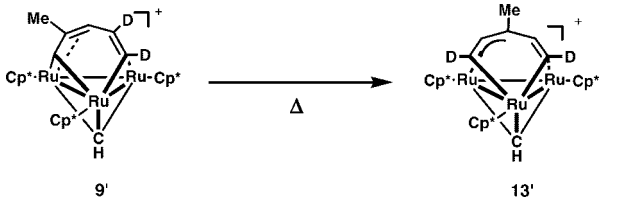
Although the ruthenacyclohexadienyl moiety is asymmetrical in the solid state, the rapid equilibrium between the two tautomers in solution (Scheme 3) exhibited a time-averaged spectrum; this indicated a symmetrical structure with a pseudomirror plane bisecting the Ru_3 plane through the Ru(1), C(1), C(4), and C(7) atoms. Two signals for the Cp* groups are observed at δ 1.83 and 1.67 in the intensity ratio of 2:1, and only two doublets, assignable to the methine protons of the ruthenacyclohexadienyl moiety, appeared at δ 7.99 and 4.21 (J_{H-H} = 5.2 Hz) at ambient temperature. The line shapes of these ^1H signals were still sharp even at −80 °C.

We examined the thermolysis of the labeled compounds **9′** and **9″**, which were prepared by the reaction of C_2D_2 and $^{13}C_2H_2$, respectively, to gain mechanistic insight into the isomerization. The thermolysis of **9′** afforded **13′**, which had a

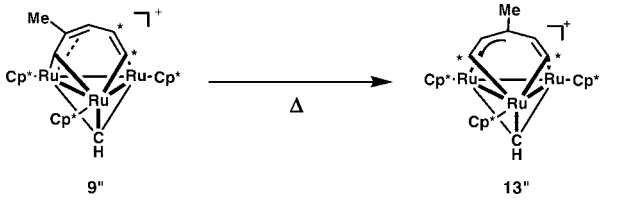
Scheme 4. Plausible Mechanism for the Skeletal Rearrangement of 9



2,6-d_2-ruthenacyclohexadienyl moiety in the molecule (eq 5). The thermolysis of **9″** also selectively yielded **13″**, in which the ^{13}C atoms were located at the 2- and 6-positions of the ruthenacyclohexadienyl moiety (eq 6). These results clearly showed that the carbon−carbon double bond of **9** that originated from acetylene was selectively split under thermal conditions.



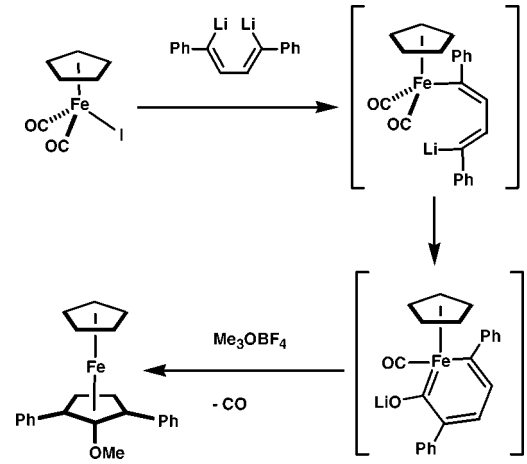
(5)



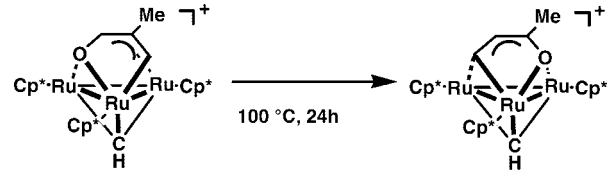
(6)

We have already reported several unprecedented skeletal rearrangements of five-membered metallacycles on a triruthenium core, namely, the isomerization of the oxaruthenacycle complex **8**[3] (eq 7) and that of the *nido*-ruthenacyclopentadiene complex **15**[12] (eq 8). On the basis of their activation parameters, $\Delta H^{\ddagger}$ 29.0 ± 0.8 kcal mol^{-1} and $\Delta S^{\ddagger} = 1.1 \pm 2.4$ eu for the isomerization of **8**[3] and $\Delta H^{\ddagger} = 26.2 \pm 2.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 8.6 \pm 0.4$ eu for that of **15**, these reactions are proved to be intramolecular.[12] The kinetic studies for the isomerization of **9** revealed that the reaction is first-order in the concentration of **9**, and the activation parameters are estimated as $\Delta H^{\ddagger}$ 32.4 ± 0.5 kcal mol^{-1} and $\Delta S^{\ddagger} = 9.8 \pm 1.4$ eu. These values are comparable to those obtained for the above-mentioned isomerization of **8** and **15**. The small absolute value of $\Delta S^{\ddagger}$ indicates that the rearrangement from **9** to **13** proceeds via intramolecular pathways. A plausible reaction path for the isomerization of **9**, which involves a μ_3-cyclopentadienyl intermediate **17**, is shown in Scheme 4. The reductive C−C coupling between C^2 and C^6 in **9** affords **17**, and the subsequent oxidative cleavage of the C^5−C^6 bond yields **13**. The structure of **17** was rationalized by

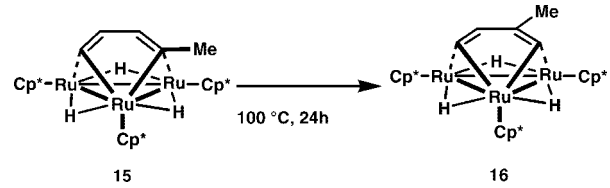
Scheme 5. Formation of a Substituted η^5-Cyclopentadienyl Group via the Formation of a Six-Membered Metallacycle Intermediate[14b]



the structurally characterized trirhodium complex $(CpRh)_3(\mu_3\text{-}C_5H_5)(\mu_3\text{-}H)$,[13] which contains a μ_3-cyclopentadienyl ligand.



(7)



(8)

As shown in Scheme 5, a metallabenzene intermediate has been often proposed for the formation of a substituted η^5-cyclopentadienyl ligand.[14,15] Although the reactivity of a

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

(13) (a) Fischer, E. O.; Mills, O. S.; Paulus, E. F.; Wawerisk, H. *J. Chem. Soc., Chem. Commun.* **1967**, 643–644. (b) Mills, O. S.; Paulus, E. F. *J. Organomet. Chem.* **1968**, *11*, 587–594.

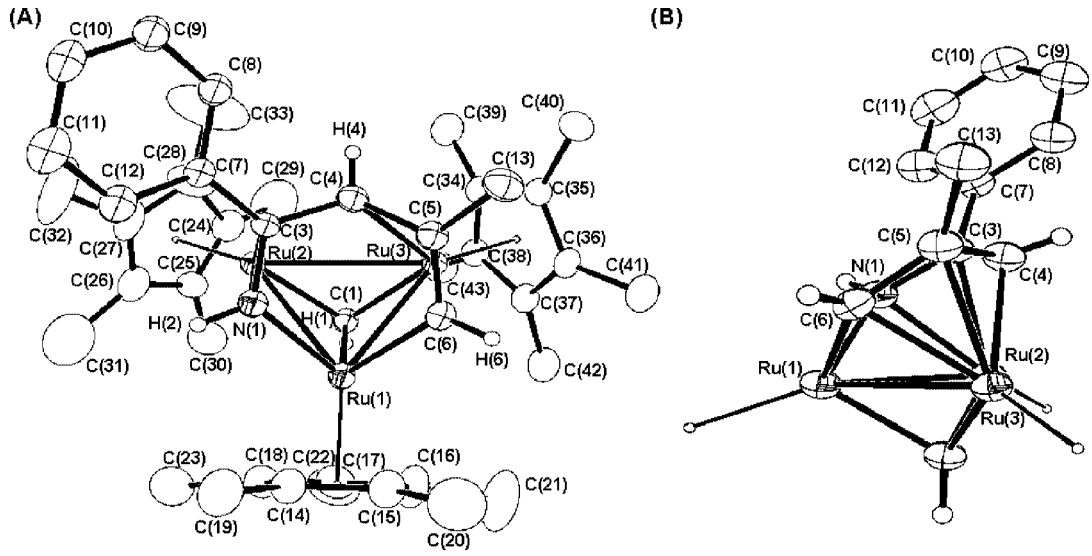
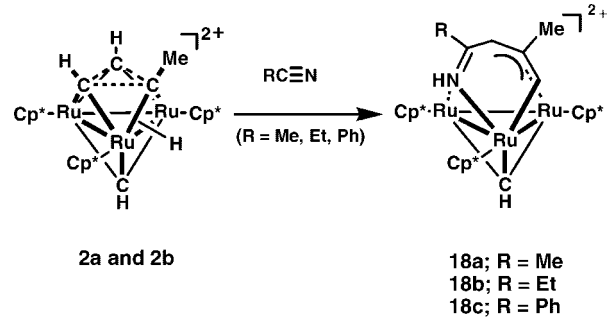


Figure 4. Molecular structure and labeling scheme of **18c** with thermal ellipsoids at the 40% probability level. The anionic moiety (PF_6^-) is omitted for clarity.

metallabenzene complex with O_2, H_2, dienophiles, and unsaturated metal species has been elucidated,[16] there are few reports on the direct observation of the reductive C−C bond formation that lead to the formation of an η^5-cyclopentadienyl ligand from a six-membered metallacycle. The isomerization of **9** to **13** via the μ_3-cyclopentadienyl intermediate would provide conclusive evidence for the cyclization step.

To complete the isomerization, rotation of the μ_3-cyclopentadienyl ligand is required prior to the C−C bond cleavage. The fluxionality of the μ_3-cyclopentadienyl ligand in **17** is reasonable by analogy with a trirhodium μ_3-cyclopentadienyl complex, $(CpRh)_3(\mu_3\text{-}C_5H_5)(\mu_3\text{-}H)$.[13]

With regard to the insertion of acetylene into a Ru−C bond, the reaction of the mixture of **2a** and **2b** with nitriles was then examined. A dicationic 2-azaruthenacyclopentadienyl complex, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^2\text{:}\eta^3\text{-}NH{=}CR{-}CHCMeCH{-})\}(\mu_3\text{-}CH)]^{2+}$ (**18a**: R = Me, **18b**: R = Et, **18c**: R = Ph), was generated by the treatment of the mixture of **2a** and **2b** with nitriles via the insertion of the nitrile group into a Ru−C bond (eq 9). The insertion of a nitrile molecule into a metal–carbon bond has been sometimes observed for metal-alkyl, metal-alkylidene, and metal-alkylidyne complexes with an electron-deficient metal center, particularly early metals.[17] However, there are still limited examples involving group VIII metals.[18] While it has been known that a nitrile molecule often inserts into an M−H bond to form an alkylidineamide ligand,[19] a nitrile molecule exclusively inserts into an M−C bond of **2** to afford **18** in this reaction.



(9)

In contrast to the reaction with acetylene, the elimination of the hydrido ligand as a proton did not occur. Instead, the hydride migrated to the nitrogen atom to form an N−H bond. In the ^1H NMR spectrum of **18a**, a broad signal assignable to an N−H bond was observed at δ 9.52, which immediately disappeared upon addition of CD_3OD. The formation of an N−H bond was also unambiguously represented by the absorption band appearing at 3289 cm^{-1} in the IR spectrum.

An X-ray diffraction study of **18c**, which was obtained by the reaction of **2** with benzonitrile, clearly indicated the presence of the μ_3-2-azaruthenacyclohexadienyl moiety as well as the dicationic nature of **18** (Figure 4). The relevant bond lengths and angles are listed in Table 1.

The triruthenium core of **18** is similar to an isosceles triangle, unlike that of **9**; the Ru−Ru bond lengths are 2.9616(4), 2.7258(4), and 2.7414(4) Å. The azaruthenacycle moiety of **18c** adopts a boat conformation, as found in **9** and **13**.

The bond distance between N(1) and C(3) is 1.372(4) Å; this value is in between that of a C=N double bond (1.28 Å) and a C−N single bond (1.45 Å) and is consistent with the π-coordination of the imine moiety to Ru(2). The bond distances of the allylic moiety C(4)−C(5) (1.458 (6) Å) and C(5)−C(6) (1.393 (6) Å) indicate the π-coordination of the three carbon atoms to Ru(3).

(14) (a) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808–6809. (b) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463–465. (c) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Organometallics* **1985**, *4*, 614–616. (d) Cantrell, R. D.; Shevlin, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 2348–2349.

(15) (a) Aime, S.; Milone, L.; Sappa, E.; Tiripicchio, J. *J. Chem. Soc., Dalton Trans.* **1977**, 227–232. (b) Blake, A. J.; Haggitt, J. L.; Johnson, B. F. G.; Parsons, S. *Dalton* **1997**, 991–994. (c) Sappa, E.; Tiripicchio, A.; Lanfredi, A. M. M. *J. Chem. Soc., Dalton Trans.* **1978**, 552–556.

(16) Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271–277.

(17) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299–338.

(18) (a) Klose, A.; Solari, E.; Ferguson, R.; Floriani, C. *Organometallics* **1993**, *12*, 2412–2416. (b) Baya, M.; Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2005**, *24*, 1225–1232.

(19) (a) See, for example: Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299–338. (b) De Bellefon, C.; Fouilloux, P. *Catal. Rev., Sci. Eng.* **1994**, *36*, 459–506. (c) Storhoff, B. N.; Lewis, H. C., Jr *Coord. Chem. Rev.* **1977**, *23*, 1–29, and references therein.

A series of bimetallic complexes having a μ-η^3-2-azametallacyclohexadienylligand,$M_2(CO)_6(\mu$-η^3-NR═CH−CHCRCR−)-(M = Fe and Ru) have been synthesized by Geoffroy's group and Elsevier's group.[20,21] The release of pyrrole from the diiron center of $Fe_2(CO)_6(\mu$-η^3-NR′═CH−CHCRCR−) has been observed upon thermolysis or oxidation using $AgBF_4$.[20a] In contrast to the diiron complex, **18** was inert to thermolysis; this is probably due to the trimetallic skeleton of **18**, namely, the C_4N ligand was tightly bound to the three ruthenium atoms.

If the μ_3-azaruthenacycle complex **18** underwent isomerization in a similar manner to that of the μ_3-ruthenacyclohexadienyl complex **9**, it would afford a μ_3-3-aza-4-phenylruthenacycle complex. However, such an isomerization did not occur upon thermolysis. This was probably due to the difficulty in forming a μ_3-pyrrole intermediate. The formation of a μ_3-pyrrole intermediate would be suppressed by the steric repulsion between the Cp* groups and the substituents on the azacycle.

Summary and Conclusion

Reactions of the dicationic triruthenium complex **2**, having a μ_3-η^3-C_3 ring, with acetylene and nitriles were examined. These reactions afforded novel six-membered metallacycles on the trimetallic core, monocationic μ_3-ruthenacyclopentadienyl complex **9** and dicationic μ_3-2-azaruthenacyclohexadienyl complex **18**, as a result of the insertion of acetylene or nitrile into a Ru−C bond.

The reaction probably proceeds via the initial formation of the dicationic μ_3-diruthenaallyl intermediate **3**. Subsequently, acetylene or the nitrile coordinates in an η^2-fashion to the dicationic metal centers. The dicationic nature of the intermediate would enhance the nucleophilic attack of the terminal carbon of the diruthenaallyl moiety on the π-coordinated acetylene or nitrile molecule.

During the formation of **9**, the hydrido ligand is eliminated as a proton. The protonation of **9**, which yields a dicationic μ_3-ruthenacyclohexadienyl complex **10**, strongly supports this mechanism. In the case of **18**, due to the presence of lone-pair electrons on the nitrogen atom, migration of the hydride to the nitrogen atom occurred instead of deprotonation.

In this study, we have shown that the skeletal rearrangement of the μ_3-ruthenacyclohexadienyl complex **9** to **13** proceeds via the formation of the μ_3-cyclopentadienyl intermediate **17** based on labeling experiments and kinetic studies. This result supports the intermediacy of a six-membered metallacycle in the formation of the η^5-cyclopentadienyl complex in the reaction of a metallacyclobutadiene complex with an alkyne.[14]

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. Acetonitrile, propionitrile, and benzonitrile were degassed and stored under an argon atmosphere. Other materials used in this research were used as purchased. The mixture of dicationic complexes **2a**,**b** was prepared according to a previously published method in ref 2, namely, treatment of μ_3-methylidyne-μ_3-η^3-2-methyldiruthenaallyl complex $(Cp^*Ru)_3(\mu_3$-CH)$(\mu_3$-η^3-CHCMeCH)$(\mu$-H) (**1**)[1] with 2 equiv of ferrocenium salt. IR spectra were recorded on a Nicolet AVATAR 360 ESP spectrophotometer. ^{1}H, ^{2}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 2400 II series CHN analyzer.

X-ray Structure Determination. X-ray-quality crystals of **9**-PF_6, **13**-BPh_4, and **18c**-PF_6 were obtained from the preparations described below and mounted on glass fibers. Diffraction experiments of **9**-PF_6, **13**-BPh_4, and **18c**-PF_6 were performed on a Rigaku RAXIS-RAPID imaging plate with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at −20 °C. The structures of **9**, **13**, and **18** 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 were refined isotropically. Neutral atom scattering factors were obtained from the standard sources.[22] Crystal data and results of the analyses are listed in Table 2.

Preparation of a Hexafluorophosphate Salt of $[(Cp^*Ru)_2$-$\{Cp^*Ru(\mu_3$-η^2:η^2-CHCMe═CH−CH═CH−$)\}(\mu_3$-CH)$]^+$ (9). Dichloromethane (10 mL) and an equilibrated mixture of hexafluorophosphate salts of the dicationic μ_3-η^3-C_3 complexes $[(Cp^*Ru)_3(\mu_3$-CH$)(\mu_3$-η^3-$C_3MeH_2)(\mu$-H$)]^{2+}$ (**2a** and **2b**, 115.9 mg, 0.109 mmol) were charged in a reaction flask. After the solution was frozen in a liquid nitrogen bath, the reaction flask was degassed by the vacuum line. Then, 1 atm of acetylene was introduced into the reaction flask at 25 °C. The solution was vigorously stirred for 3 h at 25 °C. The color of the solution changed from brown to red. After the solvent was removed under reduced pressure, the residual solid was dissolved in 2 mL of THF. The ^{1}H NMR spectrum of the residual solid showed the exclusive formation of **9**. In order to remove the liberated acid, the residual solid was then purified by the use of column chromatography on alumina (Merck, Art. No. 1097) with THF. Removal of the solvent under reduced pressure afforded a hexafluorophosphate salt of **9** (76.8 mg, 0.0812 mmol) as a brownish-red solid (75% yield). A single crystal used for the diffraction studies was prepared from the methanol solution of a hexafluorophosphate salt of **9** stored at −30 °C. Due to low solubility of **9**-PF_6 in acetone-d_6, the ^{13}C NMR spectrum of **9** was recorded using a tetraphenylborate salt of **9**, which was obtained by adding a large excess amount of $NaBPh_4$ (ca. 10 equiv) to a methanol solution of **9**-PF_6. ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ 1.71 (s, 15H, C_5Me_5), 1.84 (s, 15H, C_5Me_5), 1.87 (s, 15H, C_5Me_5), 2.44 (s, 3H, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H−), 2.94 (ddd, 1H, J_{H-H} = 6.0, 2.4, 2.0 Hz, μ_3-C^2HC^3Me═C^4H-C^5H═C^6H−), 4.09 (dd, 1H, J_{H-H} = 6.0, 5.6 Hz, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H−), 7.94 (d, 1H, J_{H-H} = 2.4 Hz, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H−), 8.08 (dd, 1H, J_{H-H} = 5.6, 2.0 Hz, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H-), 16.24 (s, 1H, μ_3-CH). ^{13}C NMR (100 MHz, 23 °C, acetone-d_6): δ 10.6 (q, J_{C-H} = 127 Hz, C_5Me_5), 11.1 (q, J_{C-H} = 127 Hz, C_5Me_5), 11.7 (q, J_{C-H} = 127 Hz, C_5Me_5), 21.7 (q, J_{C-H} = 127 Hz, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H−), 42.3 (d, J_{C-H} = 162 Hz, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H−), 61.9 (d, J_{C-H} = 163 Hz, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H−), 69.5 (s, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H−), 95.9 (s, C_5Me_5), 96.2 (s, C_5Me_5), 101.8 (s, C_5Me_5), 122.2 (d, J_{C-H} = 156 Hz, BPh_4), 125.9 (d, J_{C-H} = 153 Hz, BPh_4), 137.0 (d, J_{C-H} = 153 Hz, BPh_4), 177.3 (d, J_{C-H} = 158 Hz, μ_3-C^2HC^3Me═C^4H−C^5H═C^6H−), 179.0 (d, J_{C-H} = 156 Hz, μ_3-C^2HC^3Me═C^4H-C^5H═C^6H−), 328.8 (d, J_{C-H} = 167 Hz, μ_3-CH). ^{1}H−^{1}H COSY: δ 2.94-δ 4.09, δ 4.09-δ 8.08. HMQC: δ_H 2.44-δ_C 21.7, δ_H 2.94-δ_C 42.3, δ_H 4.09-δ_C 61.9, δ_H 7.94-δ_C

(20) (a) Snead, T. E.; Mirkin, C. A.; Lu, K.-L.; Beckman, H. L.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1992**, *11*, 942–954. (b) Mirkin, C. A.; Oyer, T. J.; Wrighton, M. S.; Snead, T. E.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1992**, *114*, 1256–1263.

(21) Mul, W. P.; Elsevier, C. J.; Vuurman, M. A.; Smeets, W. J. J.; Spek, A. L.; de Poer, J. L. *J. Organomet. Chem.* **1997**, *532*, 89–100.

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

Table 2. Crystallographic Data for 9-PF_6, 13-BPh_4, and 18c-PF_6

	9-PF_6	13-BPh_4	18c-PF_6
	(a) Crystal Data		
empirical formula	$C_{37}H_{53}F_6PRu_3$	$C_{61}H_{73}BRu_3$	$C_{42}H_{57}F_{12}NP_2Ru_3$
fw	945.97	1120.21	1169.04
cryst descrip	platelet	block	platelet
cryst color	red	red	red
cryst size (mm)	0.30 × 0.30 × 0.05	0.30 × 0.25 × 0.25	0.40 × 0.10 × 0.10
crystallizing solution	MeOH (−30 °C)	MeOH/THF (4 °C)	MeOH (−30 °C)
cryst syst	orthorhombic	triclinic	monoclinic
space group	*Pbca* (#61)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)
lattice parameters	a = 17.9482(5) Å	a = 11.3369(5) Å	a = 13.6292(3) Å
	b = 19.5298(4) Å	b = 13.8483(7) Å	b = 20.4878(4) Å
	c = 20.9501(4) Å	c = 17.3975(7) Å	c = 16.4835(4) Å
		α = 70.706(2)°	
		β = 86.346(3)°	β = 102.2440(12)°
		γ = 82.1480(19)°	
V (Å^3)	7343.5(3)	2553.3(2)^3	4498.03(17)
Z value	8	2	4
D_{calc} (g/cm^3)	1.711	1.457	1.726
measurement temp (°C)	−20	−20	−20
μ(Mo Kα) (mm^{-1})	1.318	0.914	1.147
	(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 reflns collected	77 167	29 437	49 178
no. of indep reflns	11 638 (R_{int} = 0.0506)	14 561 (R_{int} = 0.0323)	13 383 (R_{int} = 0.0462)
no. of reflns obsd (>2σ)	6937	12 377	9532
abs corr type	empirical	empirical	empirical
abs transmn	0.8818 (min.),	0.8611 (min.),	0.6569 (min.),
	1.1208 (max.)	1.1576 (max.)	0.9449 (max.)
	(c) Refinement (SHELXL-97-2)		
R_1 (I > 2σ(I))	0.0369	0.0390	0.0454
wR_2 (I > 2σ(I))	0.0815	0.0871	0.1063
R_1 (all data)	0.0652	0.0503	0.0702
wR_2 (all data)	0.0875	0.0933	0.1168
no. of data/restraints/params	10 723/0/461	14 511/0/623	13 016/0/574
GOF	0.892	1.113	1.021
largest diff peak and hole (e·Å^{-3})	0.959 and −0.748	0.766 and −1.081	0.770 and −1.206

177.3, δ_H 8.08-δ_C 179.0. IR (ATR): 836, 874, 911, 1021, 1053, 1092, 1134, 1272, 1321, 1377, 1450, 1476, 1640, 2906 (cm^{-1}). Anal. Calcd for $C_{37}H_{53}PF_6Ru_3$: C, 46.98; H, 5.65. Found: C, 46.99; H, 5.60.

Preparation of a Hexafluorophosphate Salt of [(Cp*Ru)$_2${Cp*Ru(μ_3-η^2:η^2-CHCMe=CH−CD=CD−)}(μ_3-CH)]$^+$ (9′). Dichloromethane (2 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_3MeH_2)(μ-H)]$^{2+}$ (**2a** and **2b**, 15.3 mg, 0.0144 mmol) were charged in a glass tube equipped with a Teflon valve. After the solution was frozen in a liquid nitrogen bath, the reaction flask was degassed by the vacuum line. Then, 1 atm of deuterated acetylene was introduced into the flask at 25 °C. The solution was vigorously stirred for 10 h at 25 °C. The solvent was removed under reduced pressure. Exclusive formation of **9′** was confirmed by the ^{1}H, ^{2}H, and ^{13}C NMR analyses. ^{1}H NMR (400 MHz, 23 °C, methanol-d_4): δ 1.69 (s, 15H, C_5Me_5), 1.81 (s, 15H, C_5Me_5), 1.84 (s, 15H, C_5Me_5), 2.42 (s, 3H, μ_3-C^2HC^3Me=C^4H−C^5D=C^6D−), 2.94 (d, 1H, J_{H-H} = 2.0 Hz, μ_3-C^2HC^3Me=C^4H-C^5D=C^6D−), 7.87 (d, 1H, J_{H-H} = 2.0 Hz, μ_3-C^2HC^3Me=C^4H−C^5D=C^6D−), 16.12 (s, 1H, μ_3-C*H*). ^{13}C{1H} NMR (100 MHz, 23 °C, methanol-d_4): δ 10.6 (C_5Me_5), 11.1 (C_5Me_5), 11.7 (C_5Me_5), 21.7 (μ_3-C^2HC^3Me = C^4H−C^5D=C^6D−), 42.7 (μ_3-C^2HC^3Me=C^4H−C^5D=C^6D−), 61.9 (t, J_{C-D} = 23 Hz, μ_3-C^2HC^3Me=C^4H−C^5D=C^6D−), 69.5 (μ_3-C^2HC^3Me=C^4H−C^5D=C^6D−), 95.9 (C_5Me_5), 96.9 (C_5Me_5), 102.1 (s, C_5Me_5), 177.3 (μ_3-C^2HC^{3}Me=C^4H−C^5D=C^6D−), 179.0 (t, J_{C-D} = 25 Hz, μ_3-C^2H−C^3Me=C^4H−C^5D=C^6D−), 328.8 (μ_3-C*H*). ^{2}H NMR (61 MHz, 23 °C, dichloromethane): δ 3.94 (μ_3-C^2HC^3Me=C^4H−C^5D=C^6D−), 7.99 (μ_3-C^2HC^3Me=C^4H−C^5D=C^6D-).

Preparation of a Hexafluorophosphate Salt of [(Cp*Ru)$_2$-{Cp*Ru(μ_3-η^2:η^2-CHCMe=CH−^{13}CH=^{13}CH−)}(μ_3-CH)]$^+$ (9″). Dichloromethane (2 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_3MeH_2)(μ-H)]$^{2+}$ (**2a** and **2b**, 20.8 mg, 0.0195 mmol) were charged in a glass tube equipped with a Teflon valve. After the solution was frozen in a liquid nitrogen bath, the reaction flask was degassed by the vacuum line. Then, 1 atm of $^{13}C_2H_2$ was introduced into the flask at 25 °C. The solution was vigorously stirred for 10 h at 25 °C. The solvent was removed under reduced pressure. Exclusive formation of **9″** was confirmed by the ^{1}H and ^{13}C NMR analyses. ^{1}H NMR (400 MHz, 23 °C, methanol-d_4): δ 1.71 (s, 15H, C_5Me_5), 1.84 (s, 15H, C_5Me_5), 1.87 (s, 15H, C_5Me_5), 2.44 (s, 3H, μ_3-C^2HC^3Me = C^4H−*C^5H=*C^6H−), 2.94 (ddd, 1H, J_{H-H} = 6.0, 2.4, 2.0 Hz, μ_3-C^2HC^3Me=C^4H-*C^5H=*C^6H−), 4.09 (ddd, 1H, J_{C-H} = 164.0 Hz, J_{H-H} = 6.0, 5.2 Hz, μ_3-C^2HC^3Me=C^4H−*C^5H=*C^6H−), 7.94 (d, 1H, J_{H-H} = 2.0 Hz, μ_3-C^2HC^3Me=C^4H−*C^5H=*C^6H−), 8.08 (ddd, 1H, J_{C-H} = 157.6 Hz, J_{H-H} = 5.2, 2.0 Hz, μ_3-C^2HC^3Me=C^4H−*C^5H=*C^6H-), 16.24 (s, 1H, μ_3-C*H*). ^{13}C{^{1}H} NMR (100 MHz, 23 °C, methanol-d_4): δ 10.6 (C_5Me_5), 11.1 (C_5Me_5), 11.7 (C_5Me_5), 21.7 (μ_3-C^2HC^3Me = C^4H−C^5D=C^6D−), 42.3 (μ_3-C^2HC^3Me=C^4H−*C^5H=*C^6H−), 61.9 (d, J_{C-C} = 39.9 Hz, μ_3-C^2HC^3Me=C^4H−*C^5H=*C^6H−), 69.5 (μ_3-C^2HC^3Me=C^4H−*C^5H=*C^6H−), 95.9 (C_5Me_5), 96.2 (C_5Me_5), 101.8 (s, C_5Me_5), 177.3 (μ_3-C^2HC^3Me=C^4H−*C^5H=*C^6H−), 179.0 (d, J_{C-C} = 39.9 Hz, μ_3-C^2HC^3Me=C^4H−*C^5H=*C^6H−), 328.8 (μ_3-C*H*).

Protonation of 9: Preparation of Dicationic μ_3-Ruthenacyclohexadienyl Complex [(Cp*Ru)$_2${Cp*Ru(μ_3-η^2:η^2-CHCMe=CH−CH=CH−)}(μ_3-CH)(μ-H)]$^{2+}$ (10). Dichloromethane-d_2 (0.4 mL) and a hexafluorophosphate salt of the cationic μ_3-cyclohexadienylcomplex [(Cp*Ru)$_2${Cp*Ru(μ_3-η^2:η^2-CHCMe=CH−CH=CH−)}(μ_3-CH)]$^+$ (**9**, 5.2 mg, 5.5 μmol) were charged in an NMR tube. After a large excess amount of trifluoromethanesulfonic acid (25 μL, 0.28 mmol) was added to the solution, the NMR tube was shaken for 10 min at 25 °C. Exclusive formation of **10** was confirmed by the ^{1}H and ^{13}C NMR analyses. ^{1}H NMR (400 MHz, 23 °C, dichloromethane-d_2): δ –18.95 (s, 1H, Ru*H*), 1.89 (s, 15H, C$_5$*Me*$_5$), 1.93 (s, 30H, C$_5$*Me*$_5$), 2.09 (s, 3H, μ_3-C^{2}HC^3*Me* = C^{4}H−C^{5}H=C^{6}H−), 4.06 (dd, 1H, J_{H-H} = 5.6, 5.6 Hz, μ_3-C^{2}HC^{3}Me=C^{4}H−C^5*H* = C^{6}H−), 5.00 (ddd, 1H, J_{H-H} = 5.6, 2.4, 1.6 Hz, μ_3-C^{2}HC^{3}Me=C^4*H*-C^{5}H=C^{6}H−), 9.11 (dd, 1H, J_{H-H} = 5.2, 1.6 Hz, μ_3-C^{2}HC^{3}Me=C^{4}H−C^{5}H=C^6*H*-), 9.12 (d, 1H, J_{H-H} = 2.4 Hz, μ_3-C^2*H*C^{3}Me=C^{4}H−C^{5}H=C^{6}H−), 13.40 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 23 °C, dichloromethane-d_2): δ 10.1 (q, J_{C-H} = 127 Hz, C$_5$*Me*$_5$), 10.5 (q, J_{C-H} = 127 Hz, C$_5$*Me*$_5$), 10.7 (q, J_{C-H} = 127 Hz, C$_5$*Me*$_5$), 20.4 (q, J_{C-H} = 127 Hz, μ_3-C^{2}HC^3*Me* = C^{4}H−C^{5}H=C^{6}H−), 64.6 (d, J_{C-H} = 170 Hz, μ_3-C^{2}HC^{3}Me=*C*^{4}H−C^{5}H=C^{6}H−), 83.9 (s, μ_3-C^{2}H*C*^{3}Me=C^{4}H−C^{5}H=C^{6}H−), 89.9 (d, J_{C-H} = 157 Hz, μ_3-C^{2}HC^{3}Me=C^{4}H−*C*^{5}H=C^{6}H−), 104.2 (s, *C*$_5$Me$_5$), 104.3 (s, *C*$_5$Me$_5$), 106.8 (s, *C*$_5$Me$_5$), 190.6 (d, J_{C-H} = 157 Hz, μ_3-*C*^{2}HC^{3}Me=C^{4}H−C^{5}H=C^{6}H−), 194.8 (d, J_{C-H} = 161 Hz, μ_3-C^{2}HC^{3}Me=C^{4}H−C^{5}H=*C*^{6}H−), 319.7 (d, J_{C-H} = 167 Hz, μ_3-*C*H). HMQC: δ_H 4.06-δ_C 89.9, δ_H 5.00-δ_C 64.6, δ_H 9.11-δ_C 194.8, δ_H 9.12-δ_C 190.6.

Preparation of a Hexafluorophosphate Salt of [(Cp*Ru)$_2$-{Cp*Ru(μ_3-η^3:η^2-CHCHCMe-CH=CH−)}(μ_3-CH)]$^+$ (13). Acetone (10 mL) and a cationic μ_3-3-methylruthenacyclohexadienyl complex **9** (109.9 mg, 0.115 mmol) were charged in a glass autoclave. The glass autoclave was heated in an oil bath at 140 °C for 43 h with vigorous stirring. 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 THF/MeOH. Removal of the solvent under reduced pressure afforded a hexafluorophosphate salt of **13** (85.2 mg, 0.091 mmol) as a brownish-red solid (78% yield). A single crystal used for the diffraction studies was prepared from the THF/methanol solution of a tetraphenylborate salt of **13**, which was obtained by adding a large excess amount of NaBPh$_4$ (ca. 10 equiv) to a methanol solution of **13**-PF$_6$, stored at 4 °C. ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ 1.53 (s, 3H, μ_3-C^{2}HC^{3}HC^4*Me*-C^{5}H=C^{6}H−), 1.67 (s, 15H, C$_5$*Me*$_5$), 1.83 (s, 30H, C$_5$*Me*$_5$), 4.21 (d, 2H, J_{H-H} = 5.2 Hz, μ_3-C^{2}HC^3*H*C^{4}Me-C^5*H*=C^{6}H−), 7.99 (d, 2H, J_{H-H} = 5.2 Hz, μ_3-C^2*H*C^{3}HC^{4}Me-C^{5}H=C^6*H*−), 16.09 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 23 °C, acetone-d_6): δ 10.5 (q, J_{C-H} = 127 Hz, C$_5$*Me*$_5$), 11.1 (q, J_{C-H} = 127 Hz, C$_5$*Me*$_5$), 23.4 (q, J_{C-H} = 126 Hz, μ_3-C^{2}HC^{3}HC^4*Me*-C^{5}H=C^{6}H−), 67.8 (d, J_{C-H} = 161 Hz, μ_3-C^{2}H*C*^{3}HC^{4}Me-*C*^{5}H=C^{6}H−), 73.0 (s, μ_3-C^{2}HC^{3}H*C*^{4}Me-C^{5}H=C^{6}H−), 95.8 (s, *C*$_5$Me$_5$), 101.7 (s, *C*$_5$Me$_5$), 177.8 (d, J_{C-H} = 157 Hz, μ_3-*C*^{2}HC^{3}HC^{4}Me-C^{5}H=*C*^{6}H−), 327.0 (d, J_{C-H} = 161 Hz, μ_3-*C*H). ^{1}H−^{1}H COSY: δ 4.21−7.99. HMQC: δ_H 1.53−δ_C 23.4, δ_H 4.21−δ_C 67.8, δ_H 7.99−δ_C 177.8. IR (ATR): 875, 911, 1019, 1051, 1090, 1133, 1271, 1320, 1374, 1476, 1640, 2906 (cm^{-1}). Anal. Calcd for C$_{37}$H$_{53}$PF$_6$Ru$_3$: C, 46.98; H, 5.65. Found: C, 46.87; H, 5.61.

Thermolysis of 9′. Methanol-d_4 (0.4 mL) and a hexafluorophosphate salt of the deuterated cationic μ_3-cyclohexadienyl complex [(Cp*Ru)$_2${Cp*Ru(μ_3-η^2:η^2-CHCMe=CH−CD=CD−)}(μ_3-CH)]$^+$ (**9′**, 5.6 mg, 5.9 μmol) were charged in an NMR tube equipped with a J-Young valve. The NMR tube was heated in an oil bath at 170 °C for 24 h. Exclusive formation of [(Cp*Ru)$_2${Cp*Ru(μ_3-η^3:η^2-CDCHCMe-CH=CD−)}(μ_3-CH)]$^+$ (**13′**) was confirmed by the ^{1}H, ^{2}H, and ^{13}C NMR analyses. ^{1}H NMR (400 MHz, 23 °C, methanol-d_4): δ 1.53 (s, 3H, μ_3-C^{2}DC^{3}HC^4*Me*-C^{5}H=C^{6}D−), 1.66 (s, 15H, C$_5$*Me*$_5$), 1.81 (s, 30H, C$_5$*Me*$_5$), 4.86 (s, 2H, μ_3-C^{2}DC^3*H*C^{4}Me-C^5*H*=C^{6}D−), 16.09 (s, 1H, μ_3-C*H*). ^{13}C{^{1}H} NMR (100 MHz, 23 °C, methanol-d_4): δ 10.6 (C$_5$*Me*$_5$), 11.2 (C$_5$*Me*$_5$), 11.7 (C$_5$*Me*$_5$), 23.6 (μ_3-C^{2}DC^{3}HC^4*Me*-C^{5}H=C^{6}D−), 68.8 (μ_3-C^{2}D*C*^{3}HC^{4}Me-*C*^{5}H=C^{6}D−), 73.5 (μ_3-C^{2}DC^{3}H*C*^{4}Me-C^{5}H=C^{6}D−), 96.2 (*C*$_5$Me$_5$), 102.1 (s, *C*$_5$Me$_5$), 177.9 (t, J_{C-D} = 23 Hz, μ_3-*C*^{2}DC^{3}HC^{4}Me-C^{5}H=*C*^{6}D−), 327.3 (μ_3-*C*H). ^{2}H NMR (61 MHz, 23 °C, dichloromethane): δ 7.91 (μ_3-C^2*D*C^{3}HC^{4}Me-C^{5}H=C^6*D*−).

Thermolysis of 9″. Methanol-d_4 (0.4 mL) and a hexafluorophosphate salt of the deuterated cationic μ_3-cyclohexadienyl complex [(Cp*Ru)$_2${Cp*Ru(μ_3-η^2:η^2-CHCMe=CH−^{13}CH=^{13}CH−)}(μ_3-CH)]$^+$ (**9″**, 6.5 mg, 6.9 μmol) were charged in an NMR tube equipped with a J-Young valve. The NMR tube was heated in an oil bath at 170 °C for 24 h. Exclusive formation of [(Cp*Ru)$_2${Cp*Ru(μ_3-η^3:η^2-^{13}CHCHCMe-CH=^{13}CH−)}(μ_3-CH)]$^+$ (**13″**) was confirmed by the ^{1}H and ^{13}C NMR analyses. ^{1}H NMR (400 MHz, 23 °C, methanol-d_4): δ 1.53 (s, 3H, μ_3-*C^{2}HC^{3}HC^4*Me*-C^{5}H=*C^{6}H−), 1.66 (s, 15H, C$_5$*Me*$_5$), 1.81 (s, 30H, C$_5$*Me*$_5$), 4.21 (d, 2H, J_{H-H} = 5.2 Hz, μ_3-*C^{2}HC^3*H*C^{4}Me-C^5*H*=*C^{6}H−), 7.99 (dd, 2H, J_{C-H} = 163.2 Hz, J_{H-H} = 5.2 Hz, μ_3-*C^2*H*C^{3}HC^{4}Me-C^{5}H=*C^6*H*-), 16.09 (s, 1H, μ_3-C*H*). ^{13}C{^{1}H} NMR (100 MHz, 23 °C, methanol-d_4): δ 10.5 (C$_5$*Me*$_5$), 11.1 (C$_5$*Me*$_5$), 11.7 (C$_5$*Me*$_5$), 23.4 (μ_3-*C^{2}HC^{3}HC^4*Me*-C^{5}H=*C^{6}H−), 67.8 (μ_3-*C^{2}HC^{3}HC^{4}Me-*C*^{5}H=*C^{6}H−), 73.5 (μ_3-*C^{2}HC^{3}HC^{4}Me-C^{5}H=*C^{6}H−), 96.8 (*C*$_5$Me$_5$), 101.7 (s, *C*$_5$Me$_5$), 177.8 (μ_3-*C*^{2}HC^{3}HC^{4}Me-C^{5}H=*C*^{6}H−), 327.0 (μ_3-*C*H).

Kinetic Experiments of the Isomerization of 9 to 13. The hexafluorophosphate salt of **9** (18.0 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 120, 130, 150, and 160 °C. The consumption of **9** was monitored at each temperature by means of ^{1}H NMR spectroscopy, and the intensities of the resonances at δ 2.44, which were assignable to the methyl protons of the ruthenacycle moiety, were recorded periodically. At regular times, the distribution of **9** was estimated by dividing the integral value for **9** by the sum of the integral values for **9** and **13**. 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; $k_{393K} = 1.18 \times 10^{-5}$ s^{-1}, $k_{403K} = 3.07 \times 10^{-5}$ s^{-1}, $k_{423K} = 2.28 \times 10^{-4}$ s^{-1}, and $k_{433K} = 5.87 \times 10^{-4}$ s^{-1}.

Preparation of a Hexafluorophosphate Salt of [(Cp*Ru)$_2$-{Cp*Ru(μ_3-η^2:η^3-NH=CMe-CHCMeCH−)}(μ_3-CH)]$^{2+}$ (18a). Acetonitrile (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)]$^{2+}$ (**2a** and **2b**, 32.0 mg, 0.030 mmol) were charged in a reaction flask. The solution was vigorously stirred for 5 h at 25 °C. The color of the solution changed from brown to red. 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 THF/MeOH. Removal of the solvent under reduced pressure afforded a hexafluorophosphate salt of **18a** (25.3 mg, 0.023 mmol) as a dark brown solid (76% yield). ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ 1.89 (s, 15H, C$_5$*Me*$_5$), 1.90 (s, 15H, C$_5$*Me*$_5$), 2.07 (s, 15H, C$_5$*Me*$_5$), 2.58 (s, 3H, μ_3-N^{2}H=C^{3}Me-C^{4}HC^5*Me*C^{6}H−), 3.00 (s, 3H, μ_3-N^{2}H=C^3*Me*-C^{4}HC^{5}MeC^{6}H−), 3.90 (dd, 1H, J_{H-H} = 2.0, 2.0 Hz, μ_3-N^{2}H=C^{3}Me-C^4*H*C^{5}MeC^{6}H−), 8.70 (d, 1H, J_{H-H} = 2.0 Hz, μ_3-N^{2}H=C^{3}Me-C^{4}HC^{5}MeC^6*H*-), 9.52 (d, 1H, J_{H-H} = 2.0 Hz, μ_3-N^2*H*=C^{3}Me-C^{4}HC^{5}MeC^{6}H−), 17.44 (s, 1H, μ_3-C*H*). Assignment of the methyl groups on C^3 and C^5 was performed by the use of [(Cp*Ru)$_2${Cp*Ru(μ_3-

η^2:η^3-NH=C(CD_3)-CHCMeCH−)}(μ_3-CH)]$^{2+}$ (**18a-***d*$_3$), which was obtained by the reaction of **2a**,**b** with CD_3CN. In the ^{1}H NMR spectrum of **18a-***d*$_2$, the signal for the methyl group was only found at δ 2.43. Therefore, the signal found at δ 3.00 was assigned to the methyl group derived from acetonitrile, and the signal at δ 2.43 was assigned to that derived from a diruthenaallyl group. ^{13}C NMR (100 MHz, 23 °C, acetone-*d*$_6$): δ 10.5 (q, J_{C-H} = 128 Hz, C_5Me_5), 11.0 (q, J_{C-H} = 128 Hz, C_5Me_5), 11.5 (q, J_{C-H} = 128 Hz, C_5Me_5), 18.3 (q, J_{C-H} = 128 Hz, μ_3-N^{2}H=C^{3}Me-C^{4}HC^5*Me*C^{6}H−), 24.3 (q, J_{C-H} = 128 Hz, μ_3-N^{2}H=C^3*Me*-C^{4}HC^{5}MeC^{6}H−), 41.0 (d, J_{C-H} = 164 Hz, μ_3-N^{2}H=C^{3}Me-*C*^{4}HC^{5}MeC^{6}H−), 74.9 (s, μ_3-N^{2}H=C^{3}Me-C^{4}H*C*^{5}MeC^{6}H−), 93.7 (s, μ_3-N^{2}H=*C*^{3}Me-C^{4}HC^{5}MeC^{6}H−), 101.3 (s, C_5Me_5), 101.4 (s, C_5Me_5), 105.8 (s, C_5Me_5), 181.5 (d, J_{C-H} = 157 Hz, μ_3-N^{2}H=C^{3}Me-C^{4}HC^{5}Me*C*^{6}H−), 347.3 (d, J_{C-H} = 165 Hz, μ_3-*C*H). HMQC: δ_H 2.58-δ_C 18.3, δ_H 3.00-δ_C 24.3, δ_H 3.90-δ_C 41.0, δ_H 8.70-δ_C 181.5. IR (ATR): 841, 1021, 1379, 1430, 1457, 1473, 2920, 2965, 3289 (cm^{-1}). Anal. Calcd for $C_{37}H_{55}NF_{12}P_2Ru_3$: C, 40.14; H, 5.01; N, 1.27. Found: C, 39.61; H, 4.92; N, 1.32.

Preparation of a Hexafluorophosphate Salt of [(Cp*Ru)$_2$-{Cp*Ru(μ_3-η^2:η^3-NH=CEt-CHCMeCH−)}(μ_3-CH)]$^{2+}$ (18b). Propionitrile (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_3MeH_2)(μ-H)]$^{2+}$ (**2a** and **2b**, 30.0 mg, 0.028 mmol) were charged in a reaction flask. The solution was vigorously stirred for 5 h at 25 °C. After the solvent was removed under reduced pressure, the residual solid was washed three times with 3 mL of pentane. The residual solid was then dried under reduced pressure, and 28.5 mg of a hexafluorophosphate salt of **18b** was obtained as a dark brown solid (0.025 mmol, 86% yield). ^{1}H NMR (400 MHz, 23 °C, acetone-*d*$_6$): δ 1.63 (t, 3H, J_{H-H} = 7.2 Hz, μ_3-N^{2}H=C^3(CH_2CH_3)-C^{4}HC^{5}MeC^{6}H−), 1.91 (s, 30H, C_5Me_5), 2.07 (s, 15H, C_5Me_5), 2.61 (s, 3H, μ_3-N^{2}H=C^{3}Et-C^{4}HC^5*Me*C^{6}H−), 3.06 (q, 2H, J_{H-H} = 7.2 Hz, μ_3-N^{2}H=C^3(C*H*$_2$CH$_3$)-C^{4}HC^{5}MeC^{6}H−), 3.91 (s, 1H, μ_3-N^{2}H=C^{3}Et-C^4*H*C^{5}MeC^{6}H−), 8.69 (s, 1H, μ_3-N^{2}H=C^{3}Et-C^{4}HC^{5}MeC^6*H*-), 9.62 (brs, 1H, μ_3-N^2*H* = C^{3}Et-C^{4}HC^{5}MeC^{6}H−), 17.48 (s, 1H, μ_3-C*H*). ^{13}C NMR (100 MHz, 23 °C, acetone-*d*$_6$): δ 10.7 (q, J_{C-H} = 128 Hz, C_5Me_5), 11.2 (q, J_{C-H} = 127 Hz, C_5Me_5), 11.8 (q, J_{C-H} = 128 Hz, C_5Me_5), 18.3 (q, J_{C-H} = 129 Hz, μ_3-N^{2}H=C^{3}Et-C^{4}HC^5*Me*C^{6}H−), 19.0 (q, J_{C-H} = 127 Hz, μ_3-N^{2}H=C^3(CH$_2$*C*H$_3$)-C^{4}HC^{5}MeC^{6}H−), 33.0 (t, J_{C-H} = 128 Hz, μ_3-N^{2}H=C^3(*C*H$_2$CH$_3$)-C^{4}HC^{5}MeC^{6}H−), 40.7 (d, J_{C-H} = 158 Hz, μ_3-N^{2}H=C^{3}Et-*C*^{4}HC^{5}MeC^{6}H−), 75.3 (s, μ_3-N^{2}H=C^{3}Et-C^{4}H*C*^{5}MeC^{6}H−), 99.1 (s, μ_3-N^{2}H=*C*^{3}Et-C^{4}HC^{5}MeC^{6}H−), 101.6 (s, C_5Me_5), 101.7 (s, C_5Me_5), 106.1 (s, C_5Me_5), 181.8 (d, J_{C-H} = 157 Hz, μ_3-N^{2}H=C^{3}Et-C^{4}HC^{5}Me*C*^{6}H−), 347.8 (d, J_{C-H} = 166 Hz, μ_3-*C*H). IR (ATR): 799, 836, 916, 1018, 1055, 1381, 1431, 1473, 2932, 2974, 3292 (cm^{-1}).

Preparation of a Hexafluorophosphate Salt of [(Cp*Ru)$_2$-{Cp*Ru(μ_3-η^2:η^3-NH=CPh-CHCMeCH−)}(μ_3-CH)]$^{2+}$ (18c). Benzonitrile (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_3MeH_2)(μ-H)]$^{2+}$ (**2a** and **2b**, 24.8 mg, 0.023 mmol) were charged in a reaction flask. The solution was vigorously stirred for 5 h at 25 °C. After the solvent was removed under reduced pressure, the residual solid was washed three times with 3 mL of pentane. The residual solid was then dried under reduced pressure, and 23.0 mg of a hexafluorophosphate salt of **18c** was obtained as a dark brown solid (0.020 mmol, 87% yield). A single crystal used for the diffraction studies was prepared from the methanol solution of a hexafluorophosphate salt of **18c** stored at −30 °C. ^{1}H NMR (400 MHz, 23 °C, acetone-*d*$_6$): δ 1.74 (s, 15H, C_5Me_5), 1.98 (s, 30H, C_5Me_5), 2.56 (s, 3H, μ_3-N^{2}H=C^{3}Ph-C^{4}HC^5*Me*C^{6}H−), 4.67 (s, 1H, μ_3-N^{2}H=C^{3}Ph-C^4*H*C^{5}MeC^{6}H−), 7.6–7.8 (m, 3H, *Ph*), 8.11 (d, 2H, J_{H-H} = 7.2 Hz, *Ph*), 8.69 (brs, 1H, μ_3-N^2*H* = C^{3}Ph-C^{4}HC^{5}MeC^{6}H−), 8.96 (s, 1H, μ_3-N^{2}H=C^{3}Ph-C^{4}HC^{5}MeC^6*H*-), 17.50 (s, 1H, μ_3-C*H*). ^{13}C{^{1}H} NMR (100 MHz, 23 °C, acetone-*d*$_6$): δ 10.7 (C_5Me_5), 10.8 (C_5Me_5), 11.4 (C_5Me_5), 17.7 (μ_3-N^{2}H=C^{3}Ph-C^{4}HC^5*Me*C^{6}H−), 38.1 (μ_3-N^{2}H=C^{3}Ph-*C*^{4}HC^{5}MeC^{6}H−), 74.8 (μ_3-N^{2}H=C^{3}Ph-C^{4}H*C*^{5}MeC^{6}H−), 90.9 (μ_3-N^{2}H=*C*^{3}Ph-C^{4}HC^{5}MeC^{6}H−), 102.1 (s, C_5Me_5), 102.2 (s, C_5Me_5), 106.5 (s, C_5Me_5), 131.7 (*Ph*), 132.9 (*Ph*), 133.9 (*Ph*), 135.2 (*Ph*), 182.4 (μ_3-N^{2}H=C^{3}Ph-C^{4}HC^{5}Me*C*^{6}H−), 348.0 (μ_3-*C*H). IR (ATR): 835, 1020, 1075, 1156, 1223, 1319, 1378, 1431, 1450, 1570, 1604, 1655, 2920, 2961, 3314 (cm^{-1}). Anal. Calcd for $C_{42}H_{57}NF_{12}P_2Ru_3$: C, 43.15; H, 4.91; N, 1.20. Found: C, 43.63; H, 5.30; N, 1.15.

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Supporting Information Available: Results of the X-ray diffraction studies and crystallographic files of **9**-PF_6, **13-**BPh_4, and **18c-**PF_6; X-ray data are also given as CIF files. These materials are available free of charge via the Internet at http://pubs.acs.org.

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