Organometallics **2003,** *22,* 1361−1363

Bimetallic Reductive C−C Coupling Reaction Induced by Chemical Oxidation: Formation of a μ_3-C_3 Ring on a Triruthenium Cluster

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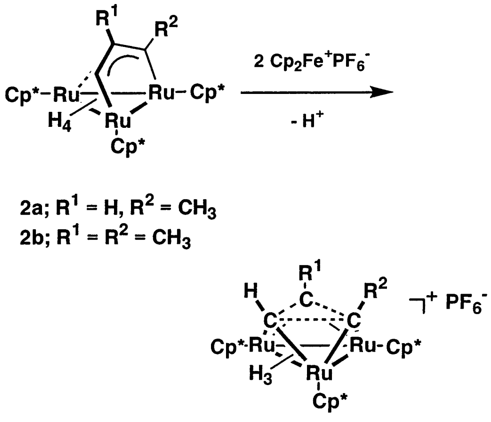
Received October 11, 2002

Summary: Oxidation of the triruthenium cluster **2** *bearing a face-bridging allyl fragment results in the formation of a* μ_3-C_3 *ring on the* Ru_3 *plane as a consequence of bimetallic reductive C−C coupling. Both structural and spectral data of* **5** *indicate carbenic character of the carbon atoms within the newly formed face-bridging* C_3 *ring.*

Since η^3 coordination of C_3Ph_3 was revealed by means of an X-ray diffraction study by Weaver and Tuggle in 1969,[1] a number of complexes containing the C_3R_3 unit have been extensively studied.[2] A variety of ring-opening[3] or ring-expansion reactions[2a−d,4] as a result of releasing the strain have been reported for some of the η^3-C_3R_3 complexes. On the other hand, formation of an η^3-C_3R_3 ring from a metallacyclobutadiene was also reported.[5] These results show that the stability based on π-conjugation is competitive with the strain of a three-membered ring. For mononuclear complexes, such a preference seems to depend mainly on the electron density of the metal centers. Due to such reversible transformation, cyclopropenyl complexes were regarded as possible intermediates in alkyne metathesis reactions as well as the isomeric metallacyclobutadiene complexes.[5]

We have studied thermal skeletal rearrangements of hydrocarbyls on a triruthenium cluster generated from $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$), in which C−H bond scission of alkane[6] and C−C bond cleavage of cyclopentadiene[7] were readily achieved as a result of cooperative action of the three adjacent ruthenium centers. Not only multiple coordination of the cluster but also multielectron transfer between the metal centers and the substrate likely plays an important role in multimetallic activation. Such multielectron transfer enables various bond activations in a manner different from those of mononuclear complexes. Thus, it is important to investigate oxidation and/or reduction. We report herein the synthesis of a triruthenium cluster containing a μ_3-C_3 ligand by chemical oxidation of the μ_3-η^3-1,3-diruthenaallyl complex $(Cp^*Ru)_3(\mu\text{-}H)_4\{\mu_3\text{-}\eta^3\text{-}C(H)C(H)CMe\}$ (**2a**),[8] which involves a novel type of C−C bond formation as a result of reductive bond coupling of a μ_3-diruthenaallyl ligand.

The reaction of **2a** with 2 equiv of $[Cp_2Fe][PF_6]$ (Fc^+; $Cp = \eta^5\text{-}C_5H_5$) quantitatively yielded the monocationic complex $[\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)][PF_6]$ (**5a**) as a brown precipitate (eq 1).[9] Oxidation of **2b** also proceeded smoothly to yield **5b**. The use of 2 molar equiv of Fc^+ is necessary to complete the reaction.



2a; R1 = H, R2 = CH3
2b; R1 = R2 = CH3

(1)

5a; R1 = H, R2 = CH3
5b; R1 = R2 = CH3

To elucidate the reaction mechanism, a solution of **2a** was subjected to a CV scan. The cyclic voltammogram of **2a** is represented in the Supporting Information

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(2) For example: (a) Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Inorg. Chem.* **1979**, *18*, 1687−1691. (b) Gompper, R.; Bartmann, E.; Nöth, H. *Chem. Ber.* **1979**, *112*, 218−233. (c) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310−1316. (d) Hughes, R. P.; Lambert, J. M.; Whitman, D. W.; Hubbard, J. L.; Henry, W. P.; Rheingold, A. L. *Organometallics* **1986**, *5*, 789−797. (e) Hughes, R. P.; Tucker, D. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3069−3074. (f) Ghilardi, C. A.; Innocenti, P.; Midollini, S.; Orlandini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1109−1113.

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(4) (a) Hughes, R. P.; Klaeui, W.; Reisch, J. W.; Mueller, A. *Organometallics* **1985**, *4*, 1761−1765. (b) Hughes, R. P.; Lambert, J. M.; Hubbard, J. L. *Organometallics* **1986**, *5*, 797−804.

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(6) (a) Matsubara, K.; Inagaki, A.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1999**, *121*, 7421−7422. (b) Inagaki, A.; Takemori, T.; Tanaka, M.; Suzuki, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 404−406.

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10.1021/om0208467 CCC: $25.00
Publication on Web 03/01/2003

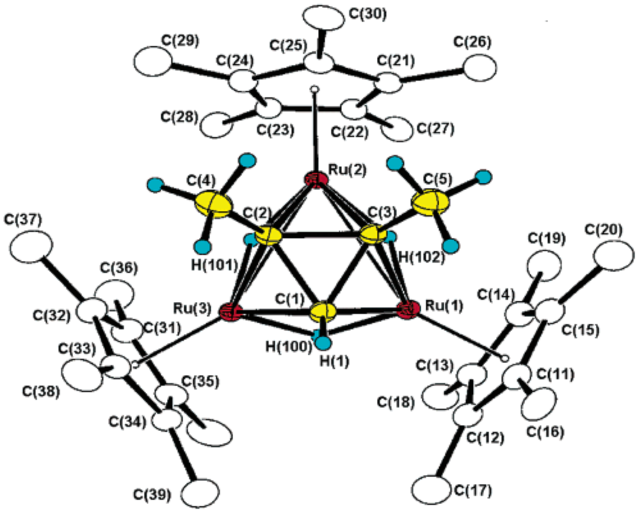
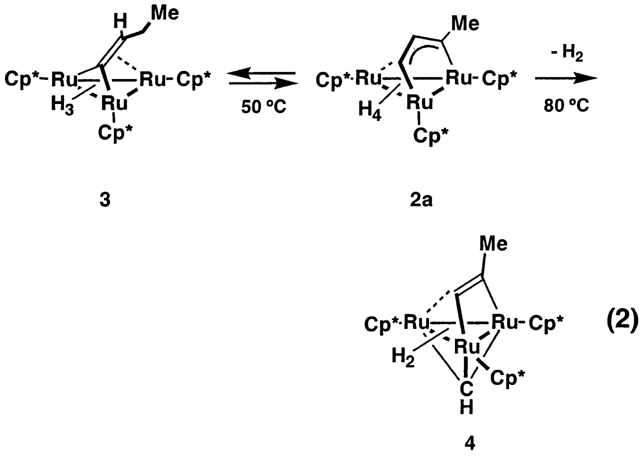


Figure 1. Molecular structure and labeling scheme of **5b** with thermal ellipsoids at the 30% probability level. The anion is neglected for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2), 2.8055(7); Ru(1)−Ru(3), 2.8145(8); Ru(2)−Ru(3), 2.8022(4); Ru(1)−C(1), 2.080(3), Ru(1)−C(3), 2.105(3); Ru(2)−C(2), 2.094(3); Ru(2)−C(3), 2.104(3); Ru(3)−C(1), 2.082(3); Ru(3)−C(2), 2.082(3); C(1)−C(2), 1.571(4); C(1)−C(3), 1.563(4); C(2)−C(3), 1.584(4); Ru(2)−Ru(1)−Ru(3), 59.815(18); Ru(1)−Ru(2)−Ru(3), 60.251(17); Ru(1)−Ru(3)−Ru(2), 59.933(14); C(2)−C(1)−C(3), 60.7(2); C(1)−C(2)−C(3), 59.4(2); C(1)−C(3)−C(2), 59.88(19).

(Figure S-1), which showed chemically quasi-reversible and irreversible one-electron waves, respectively. The quasi-reversible wave at $E_{1/2} = -776$ mV indicates the formation of a 47-electron species. The second anodic peak was observed at $E_{p,a} = -305$ mV, but the corresponding cathodic peak was relatively diminished, which implies that the second process was irreversible. Therefore, skeletal rearrangement and deprotonation most likely took place at this stage. The redox potential of Fc^+ is 159 mV vs Ag/Ag^+; thus it can be concluded that 2 molar equiv of Fc^+ readily oxidized **2a** from the neutral to the dicationic state. Since the rate of the second oxidation was probably faster than that of the first one, the 47-electron intermediate was not detected and isolated.

Decrease of electron density at the metal centers promoted reductive C−C bond formation between the two metal centers and led to the formation of complex **5**. It is quite different from the skeletal rearrangement caused by the thermolysis of **2a**. The μ_3-allyl complex **2a** is in equilibrium with the μ-vinylidene complex **3** in solution at 50 °C, and **2a** is converted to the μ_3-methylidyne, μ_3-η^2-(||)-propyne complex **4** upon heating at 80 °C as a result of C−C bond cleavage (eq 2).[8b]



Although formation of an η^3-cyclopropenyl ligand by reductive C−C bond formation of a metallacyclobutadiene ligand on a high-valent tungsten center was well established by Schrock et al.,[5] there are few examples for the formation of the μ_3-η^3-C_3R_3 ligand on cluster complexes. To the best of our knowledge, there has been only one example of a μ_3-η^3-C_3R_3 complex; Ernst et al. obtained $(Cp^*Ru)_3(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)(\mu_3\text{-}CO)$ by the reaction of $\{Cp^*Ru(\mu\text{-}Cl)\}_4$ with *trans*-3-methyl-2-butenal in the presence of K_2CO_3.[10] It is uncertain whether the C−C bond was formed on one metal center after a 1,2-shift of the terminal carbon atom or was directly formed across the two metal centers. Such types of bond-forming reactions between two metal centers have been well investigated in A-frame type complexes.[11] There is still argument regarding the mechanism, but some of the reactions were considered to proceed via a 1,2-shift of the alkyl group.

In the ^{1}H NMR spectrum of **5**, both signals for Cp* and hydride are observed as a set of two signals with an intensity ratio of 1:2, respectively. Complex **5** is stereochemically rigid, at least within the NMR time scale, and the line shape of these signals remained unchanged up to 70 °C. Although hydride signals of **5b** appeared at the same position and were observed as a single peak at 23 °C, they separated into two signals at −50 °C without showing any broadening (δ −20.22 and −20.25 in CD_3OD). Nonfluxionality of the μ_3-C_3 ligand was also reported by Ernst et al.,[10] while rotation of the η^3-cyclopropenyl ligand was often observed for mononuclear complexes.[2f,12]

The ^{1}H signals for the methine proton of **5** attached to the three-membered ring appeared at considerably lower magnetic field (**5a**, δ 6.98; **5b**, δ 6.82) than for Ernst's complex (δ 5.95),[10] which was probably due to

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(8) (a) Takemori, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 4346−4348. (b) Takemori, T.; Inagaki, A.; Suzuki, H. *J. Am. Chem. Soc.* **2001**, *123*, 1762−1763.

(9) **5a**: ^{1}H NMR (400 MHz, acetone-d_6, 23.0 °C, TMS) δ 6.98 (s, 2H, $-CH$), 2.25 (s, 3H, $-CH_3$), 1.90 (s, 30H, C_5Me_5), 1.85 (s, 15H, C_5Me_5), −19.96 (t, $J_{H-H} = 4.7$ Hz, 1H, Ru-H), −20.21 (d, $J_{H-H} = 4.7$ Hz, 2H, Ru-H); ^{13}C NMR (100 MHz, THF-d_8, 23.0 °C, TMS) δ 144.6 (s, $-CCH_3$), 140.8 (d, $J_{C-H} = 184.7$ Hz, $-CH$), 97.6 (s, C_5Me_5), 31.9 (q, $J_{C-H} = 126.7$, $-CCH_3$), 12.4 (q, $J_{C-H} = 126.7$ Hz, C_5Me_5), 12.3 (q, $J_{C-H} = 126.7$ Hz, C_5Me_5). **5b**: ^{1}H NMR (400 MHz, acetone-d_6, 23.0 °C, TMS) δ 6.82 (s, 1H, $-CH$), 2.15 (s, 6H, $-CH_3$), 1.91 (s, 30H, C_5Me_5), 1.87 (s, 15H, C_5Me_5), −20.15 (m, 3H, Ru−H); ^{13}C NMR (100 MHz, THF-d_8, 23.0 °C, TMS) δ 146.1 (d, $J_{C-H} = 180.0$ Hz, $-CH$), 145.5 (s, $-CCH_3$), 96.5 (s, C_5Me_5), 96.3 (s, C_5Me_5), 27.4 (q, $J_{C-H} = 126.7$, $-CCH_3$), 11.3 (q, $J_{C-H} = 126.7$ Hz, C_5Me_5), 11.0 (q, $J_{C-H} = 126.7$ Hz, C_5Me_5).

(10) Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1994**, *13*, 2423−2429.

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

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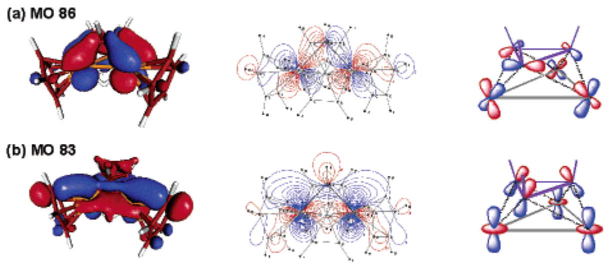

Figure 2. Molecular orbitals and contour maps of the plane defined by two ruthenium atoms and one ring carbon of (a) MO 86 and (b) MO 83 in **6**. The contours are ±0.0125, ±0.0250, ±0.0375, ±0.0500, ±0.0625, ±0.0750, ±0.0875, ±0.1000, and ±0.1125. Qualitative orbital interaction diagrams in **6** are also shown.

weaker back-donation from the cationic ruthenium centers to the ring carbons. The J_{C-H} value for the ring carbon is significantly large (**5a**, 184.7 Hz; **5b**, 180.0 Hz), and this value is the most typical feature of a μ_3-C_3 ring. However, this is smaller than the values for the mononuclear cyclopropenyl complex (η^3-C_3Ph_2H)Fe(CO)$_2$(NO) (J_{C-H} = 232 Hz) and the free cyclopropenyl cation (J_{C-H} = 262 Hz).[2d]

A single crystal of **5b** suitable for X-ray diffraction study was obtained from cold THF solution. The structure of the cationic part of **5b** is depicted in Figure 1.[13]

The C_3 plane was located nearly parallel to the Ru_3 triangle in staggered form. The average Ru−Ru distance (2.81 Å) corresponds to an Ru−Ru single bond and is slightly longer than those of $(Cp^*Ru)_3(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)(\mu_3\text{-}CO)$ (average 2.74 Å).[10] Such elongation is possibly caused by the μ_2-hydride ligands of **5b**. The average Ru−C distance of 2.094 Å for the C_3 ring is slightly longer than that of $(Cp^*Ru)_3(\mu_3\text{-}\eta^3\text{-}C_3H_2Me)(\mu_3\text{-}CO)$ (2.056 Å),[10] which also indicates weaker back-donation from the ruthenium centers of **5b**.

The three-membered carbon atom ring forms a nearly equilateral triangle with sides of 1.571(4), 1.563(4), and 1.584(3) Å, respectively. Notably, these C−C bond distances of the C_3 ring are significantly longer than the normal C−C single bond ($C(sp^3)-C(sp^3) = 1.537 \pm 0.005$ Å). As for mononuclear η^3-C_3R_3 complexes, the C−C bond lengths mostly lie in the range from 1.40 to 1.45 Å.[1,2,5] It is also characteristic of the μ_3-C_3 complexes that the bend-back angles of the substituents from the C_3 plane are significantly larger than those of mononuclear cyclopropenyl complexes; C(4), C(5), and H(1) are bent away by 53.3, 53.2, and 55.5°, respectively, while those of mononuclear complexes lie in the range from 13.7 to 43.5°.[2,5]

The very long C−C bond distance in the μ_3-C_3 ring is the most striking feature of complex **5b**. The C_3 ring coordinated to **5** is significantly different from those of mononuclear cyclopropenyl complexes in this respect. Chemical shifts of δ_H 6.82 and δ_C 146.1 and the large J_{C-H} value of 180 Hz strongly suggest the carbenic character of the ring carbons. The C_3 ring thus can be described as tris(μ-carbene) as well as μ_3-cyclopropenyl.

A density functional study on the model complex $[\{CpRu(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^3\text{-}C_3H_3)]^+$ (**6**) was carried out in order to gain deep insight into the nature of the μ_3-C_3 ring. The optimized structure of **6** exhibited reasonable agreement with the molecular structure of the cationic part of **5b**. The detailed procedure and results of the ab initio calculation are given in the Supporting Information.

MO 83 shows an overlap of the p_z orbitals of the ring carbons across the C_3 ring, which interact with the d_{z^2} orbitals of the ruthenium centers (Figure 2b). Such $\pi-\pi$ stacking-like interaction between p_z orbitals and d_{z^2} orbitals indicates the conjugated cyclopropenyl character of the C_3 ring. In contrast to this, MO 86 clearly shows a μ-carbenic interaction among the carbon atom and ruthenium centers (Figure 2a). Since the difference between the eigenvalues of MO 83 and MO 86 is so small in energy (0.019 au), the C_3 ring adopts a resonance form between μ-carbene and μ_3-cyclopropenyl. Elongation of the C−C bond of the ring carbon is most likely attributed to the interaction of d_{yz} and/or d_{zx} with antibonding orbitals of the C_3 ring in the MO 86 as well as decrease of the pπ(C−C) interaction upon coordination (MO 83). Thus, the C−C bond distances of **6** are much longer than those observed in the monometallic η^3-cyclopropenyl complexes. Large bend-back angles of the substituent on the C_3 ring are quite consistent with the μ-carbenic character of the C_3 ring carbons.

This reaction is a rare example of bimetallic reductive C−C coupling performed on a cluster induced by two-electron oxidation. We are now focusing on the mechanistic details of the formation of the C_3 ring on the Ru_3 cluster, especially in the bond-forming step.

Acknowledgment. This research was partially supported by fellowships of the Japan Society for the Promotion of Science for Japanese Junior Scientists. We thank Prof. Kentaro Yamaguchi and Dr. Shigeru Sakamoto (Chiba University) for measurement of the CSI-MS spectra. We acknowledge Kanto Chemical Co., Inc., for generous gifts of pentamethylcyclopentadiene.

Supporting Information Available: Text, tables, and figures giving synthetic details for compounds **5a** and **5b**, results of the DFT calculation for **6**, and X-ray crystallographic data for **5b**; these X-ray data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data: empirical formula $C_{35}H_{55}F_6PRu_3$, $T = 223$ K, $\lambda = 0.710\,69$ Å, space group $P2_1/n$ (No. 14), $a = 11.537(4)$ Å, $b = 14.5807(19)$ Å, $c = 22.450$ (3) Å, $\beta = 100.74(3)°$, $V = 3710.4(14)$ Å^3, $Z = 4$, $D_c = 1.65$ g/cm^3. The final structure for **5b** was refined to R1 = 0.0361 and wR2 = 0.0733 for 7751 observed reflections ($I > 2\sigma(I)$) and 440 parameters.