Thermal Skeletal Rearrangement of a *nido*-Ruthenacyclopentadiene Complex Involving Reversible Rupture and Formation of a Ruthenium−Ruthenium Bond

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Summary: *Thermolysis of a triruthenium complex containing a nido-ruthenacyclopentadiene ligand {Cp*Ru(μ-H)}$_3$(CH═CMe-CR═CH) (**3a**, R = H; **3b**, R = Me, Cp* = η^5-C$_5$Me$_5$) affords an open-form Ru$_3$ cluster (Cp*Ru)$_2$-{Cp*Ru(CH═CMe-CR═CH)}(μ-H) (**4a**, R = H; **4b**, R = Me) as a result of partial Ru−Ru bond cleavage. Reformation of an Ru$_3$ triangle accompanied with C−C bond cleavage of the C$_4$ fragment was performed by prolonged heating of **4** to afford a μ$_3$-methylidyne-μ$_3$-diruthenaallyl complex (Cp*Ru)$_3$(μ-H)(μ$_3$-CH)(μ$_3$-CRC-MeCH) (**5a**, R = H; **5b**, R = Me).*

We have demonstrated various notable methods of bond activation during our studies on the triruthenium pentahydride complex {Cp*Ru(μ-H)}$_3$(μ$_3$-H)$_2$ (**1**) with hydrocarbons.[1] Substrates once incorporated into the reaction field of the Ru$_3$ cluster have been activated effectively by synergy of the adjacent metal centers. Actually, smooth cleavage of C−H,[2] C−C,[3] and C−S bonds[4] has been achieved in the reaction field of **1**.

Firm resistance of **1** against fragmentation of the Ru$_3$ framework was confirmed by the fact that **1** did not afford any crossover products upon heating with {EtCpRu(μ-H)}$_3$(μ$_3$-H)$_2$ (EtCp = η^5-C$_5$Me$_4$Et) at 200 °C for 14 days. It was thus proven that the Ru$_3$ skeleton was tightly maintained during the reaction. However, in the reaction of **1** with linear alkanes to afford a *closo*-ruthenacyclopentadiene complex (Cp*Ru)$_2$-{Cp*Ru(CR═CHCH═CH)}(μ-H) (**2a**−**e**, R = C$_n$H$_{2n+1}$, *n* = 1−5), partial bond-breaking of the Ru$_3$ triangle was observed.[2d]

This reaction was considered to proceed via formation of an intermediary μ$_3$-alkylidyne complex. The Ru−Ru bond was thus thought to be cleaved during the skeletal rearrangement of the hydrocarbyl ligand, resulting in the formation of a ruthenacyclopentadiene fragment. The role of an M−M bond of the cluster for the multimetallic activation has not yet been clarified in detail. Only a few examples of reversible M−M bond cleavage of trinuclear complexes have been known.[5]

Knox et al. elucidated C−C bond cleavage on the cluster by thermolysis of the distorted *nido*-type complex [Ru$_3$(CO)$_2$(μ-CO)$_2${μ$_3$-C$_4$(CF$_3$)$_2$(CO$_2$Me)$_2$}(η^5-C$_5$H$_5$)$_2$].[6] In this reaction, two products were independently obtained, and one of which has been revealed to adopt an open-form *closo*-type structure. Although mechanistic details have not been established, the positions of the CF$_3$ groups in this compound indicated occurrence of the simultaneous C(CF$_3$)−C(CF$_3$) bond cleavage with an Ru−Ru bond cleavage.

In this communication, we report thermal skeletal rearrangements of the *nido*-ruthenacyclopentadiene complex {Cp*Ru(μ-H)}$_3$(CH═CMe-CR═CH) (**3a**, R = H; **3b**, R = Me) to a μ$_3$-methylidyne−μ$_3$-diruthenaallyl complex **5** by way of a *closo*-ruthenacyclopentadiene complex **4** as a result of cleavage and re-formation of one of the Ru−Ru bonds.

Thermolysis of **3a** at 130 °C for 45 h afforded a mixture of *closo*-ruthenacyclopentadiene complex (Cp*Ru)$_2${Cp*Ru(CH═CMe-CH═CH)}(μ-H) (**4a**) and μ$_3$-methylidyne−μ$_3$-diruthenaallyl complex (Cp*Ru)$_3$(μ-H)-(μ$_3$-CH)(μ$_3$-CHCMeCH) (**5a**) in the intensity ratio of 33:67 (eq 1).[7] Prolonged heating at 170 °C for 14 h resulted in a change in the **4a**/**5a** ratio to 2:98. No decomposition was observed during the reaction. Distribution of the products was followed by means of ^{1}H NMR spectroscopy in *p*-xylene-*d*$_{10}$ solution at 130 °C, which is shown in the Supporting Information (Figure S-1). With the reaction time, an increase in the intensi-

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(7) Spectral data: **4a**, ^{1}H NMR (400 MHz, benzene-*d*$_6$, 23.0 °C, TMS): δ 4.61 (d, J_{H-H} = 4.4 Hz, 1H, C^3*H*), 4.34 (s, 1H, C^1*H*), 4.18 (d, J_{H-H} = 4.4 Hz, 1H, C^4*H*), 2.47 (s, 3H, −C^{2}C*H*$_3$), 2.27 (s, 15H, C$_5$*Me*$_5$), 1.83 (s, 15H, C$_5$*Me*$_5$), 1.64 (s, 15H, C$_5$*Me*$_5$), −10.20 (s, 1H, Ru-*H*). **4b**, ^{1}H NMR (500 MHz, benzene-*d*$_6$, 23.0 °C, TMS): δ 4.29 (s, 2H, C^1*H* and C^4*H*), 2.68 (s, 6H, −C^{2}C*H*$_3$ and −C^{3}C*H*$_3$), 2.24 (s, 15H, C$_5$*Me*$_5$), 1.77 (s, 15H, C$_5$*Me*$_5$), 1.61 (s, 15H, C$_5$*Me*$_5$), −10.13 (s, 1H, Ru-*H*). **5a**, ^{1}H NMR (400 MHz, benzene-*d*$_6$, 23.0 °C, TMS): δ 16.15 (s, 1H, μ$_3$-C*H*), 8.24 (s, 2H, C^1*H* and C^3*H*), 2.29 (s, 3H, C^{2}C*H*$_3$), 1.90 (s, 30H, C$_5$*Me*$_5$), 1.58 (s, 15H, C$_5$*Me*$_5$), −22.45 (s, 1H, Ru*H*). **5b**, ^{1}H NMR (400 MHz, benzene-*d*$_6$, 23.0 °C, TMS): δ 16.14 (s, 1H, μ$_3$-C*H*), 8.24 (s, 1H, C^1*H*), 2.23 (s, 3H, C^{2}C*H*$_3$), 1.92 (s, 15H, C$_5$*Me*$_5$), 1.90 (s, 15H, C$_5$*Me*$_5$), 1.60 (s, 3H, C^{3}C*H*$_3$), 1.58 (s, 15H, C$_5$*Me*$_5$), −22.44 (s, 1H, Ru*H*).

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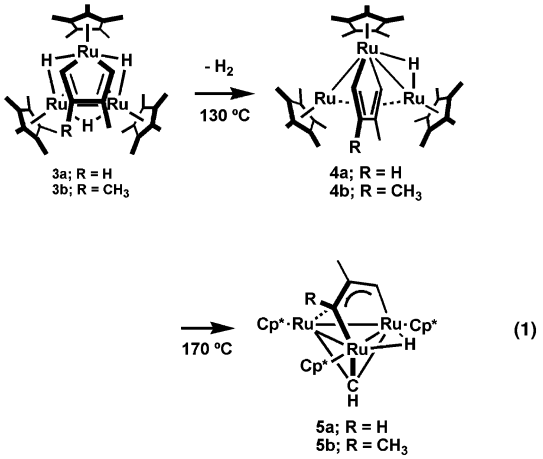

(1)

ties of the signals for **4a** and **5a** and a significant decrease in that of **3a** were observed. After 40 h, the signal attributable to **3a** disappeared and the yield of **4a** reached its maximum value of 37%. Then, the intensity of the signals for **4a** began to decrease and the yields of **4a** and **5a** reached 32 and 68%, respectively, after 60 h. These facts clearly showed that **5a** was formed via the formation of **4a** as an intermediate.

Complex **4a** was isolated from the reaction mixture with column chromatography on alumina and was definitely identified as the *closo*-ruthenacyclopentadiene complex $(Cp^*Ru)_2\{Cp^*Ru(CH{=}CMeCH{=}CH)\}(\mu\text{-H})$ on the basis of ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum, three Cp* signals with the same intensity were observed at δ 2.27, 1.83, and 1.64. The resonance assignable to the hydride appeared at δ −10.23 as a singlet. The ^1H signals attributable to the ruthenacyclopentadiene moiety were observed at δ 4.61 (d, J_{H-H} = 4.4 Hz), 4.34 (s), and 4.18 (d, J_{H-H} = 4.4 Hz). The signals of the carbons attached to the central ruthenium atom appeared at δ 115.8 (d, J_{C-H} = 149.0 Hz) and 122.1 (d, J_{C-H} = 154.1 Hz). These results implied the carbenic character of the α-carbons of the ruthenacyclopentadiene moiety. These spectral data were very similar to those of **2**, which was formed by the reaction of **1** with *n*-alkane.[2d]

Thermolysis of **3b** in heptane at 170 °C for 9 h also afforded a mixture of **4b** and **5b** in the intensity ratio of 78:22. In contrast to the thermolysis of **3a**, the *closo*-ruthenacyclopentadiene complex **4b** was a major product. Further transformation of **4b** to **5b** also took place, but it required longer reaction time than that required for the formation of **4a**. This was probably due to the steric demand of the additional methyl group on the ruthenacyclopentadiene moiety, which seems to suppress the transformation from **4** to **5**.

A red single crystal of **4b** suitable for X-ray diffraction studies was obtained from a cold Et_2O/THF (5:1) solution of the mixture. An ORTEP diagram of **4b** is depicted in Figure 1, which clearly shows an open form of the Ru_3 core.[8] While the bond lengths of Ru(1)−Ru(2) and Ru(1)−Ru(3) (2.7949(5) and 2.7847(5) Å, respectively) are within an Ru−Ru single bond, the distance between Ru(2) and Ru(3) (3.7326 Å) is considerably longer. The position of the hydride ligand could not be located, but lack of the apparent absorption band of the stretching vibration, ν(Ru−H), in the IR spectra of **4** implies that it bridges between one of the

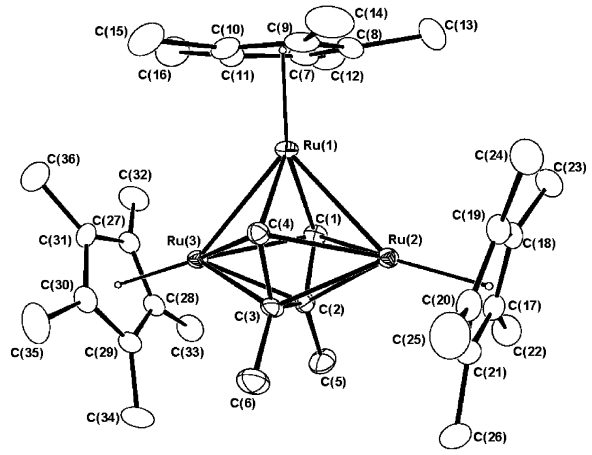

Figure 1. Molecular structure of **4b** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Ru(1)−Ru(2), 2.7949(5); Ru(1)−Ru(3), 2.7847(5); Ru(1)−C(1), 2.047(4); Ru(1)−C(4), 2.070(4); C(1)−C(2), 1.457(5), C(2)−C(3), 1.469(6); C(3)−C(4), 1.448(6); Ru(2)−Ru(1)−Ru(3), 83.974(12); C(1)−Ru(1)−C(4), 76.83(16); Ru(1)−C(1)−C(2), 119.7(3); C(1)−C(2)−C(3), 112.2(3); C(2)−C(3)−C(4), 111.9(3); Ru(1)−C(4)−C(3), 119.4(3).

Ru−Ru bonds. Bond alternation was not observed in the ruthenacycle; namely, the lengths of the C(1)−C(2), C(2)−C83), and C(3)−C(4) were 1.457(5), 1.469(6), and 1.448(6) Å, respectively, which implies that the C=C double bonds were delocalized over the ruthenacyclopentadiene moiety. Coplanarity of the five atoms consisting of the ruthenacyclopentadiene fragment was confirmed by the sum of the interior angles (540.0°).

Thermolysis of **4a** at 170 °C for 14 h resulted in exclusive formation of **5a**. In the ^1H NMR spectrum of **5a**, two singlets assignable to the Cp* groups were observed at δ 1.58 and 1.90 in the intensity ratio of 1:2. This indicates that **5a** has a mirror plane bisecting the Ru_3 triangle, and thus the hydride ligand must be located on the mirror plane as a bridging ligand. All of the ^1H and ^{13}C NMR data were well consistent with its structure, and these data were similar to those of the diruthenaallyl complexes that we have already reported.[2a,9]

As mentioned above, due to its additional methyl group on the C_4 fragment, formation of **5b** requires longer reaction time. After the solution of **3b** in heptane was heated at 170 °C for 10 days, a small amount of **4b** still remained unreacted. Complex **5b** was isolated by the use of column chromatography on alumina in 38% yield as a red solid. In contrast to **4a**, three singlet signals assignable to the Cp* groups were observed at δ 1.92, 1.90, and 1.58 in the ^1H NMR spectra of **5b**. The additional methyl group at the α-position of the diruthenaallyl moiety broke the C_s symmetry adopted in **5a**.

Cleavage of the C−C bond of the ruthenacyclopentadiene moiety of **4a** was apparent in the structure of **5a** shown in Figure 2, which clearly represents the μ_3-η^1:

(8) Crystal data for **4b**: $C_{36}H_{54}Ru_3$, fw = 790.03, orthorhombic, space group *Pccn*, a = 18.440(2) Å, b = 22.5372(12) Å, c = 15.9042(18) Å, V = 6609.7(11) Å^3, Z = 8, D_{calcd} = 1.588 g/cm^3, temp −50 °C, μ(Mo Kα) = 13.76 cm^{-1}, R1 = 0.048, wR2 = 0.105 for 6750 reflections with $I > 2\sigma(I)$. Since the hydrogen atom attached to the ruthenium atom could not be located in the difference Fourier map, it was omitted.

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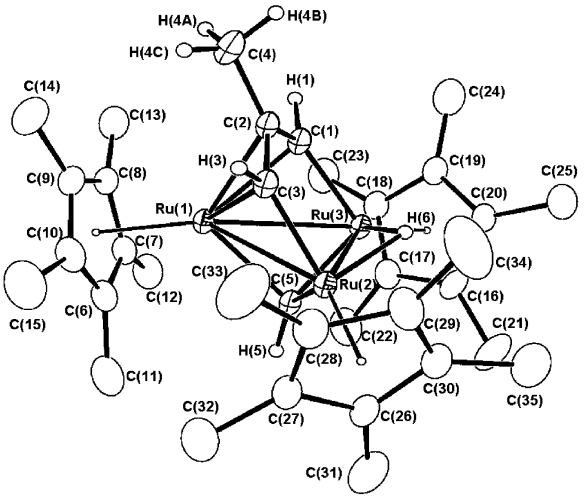
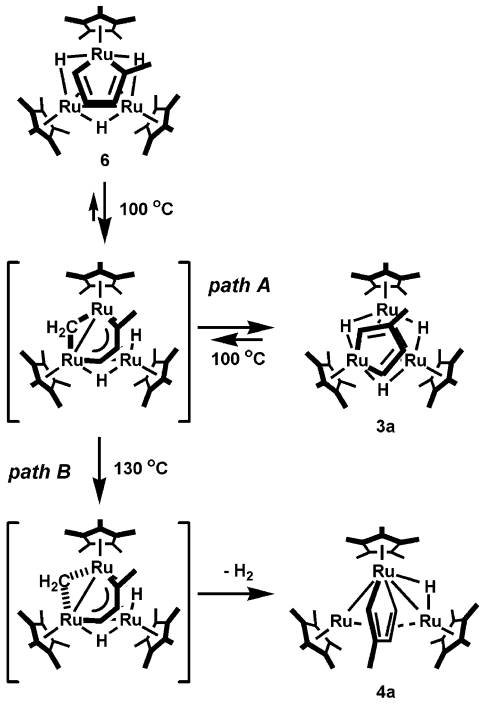


Figure 2. Molecular structure of **5a** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Ru(1)−Ru(2), 2.7261(8); Ru(1)−Ru(3), 2.7256(8); Ru(2)−Ru(3), 2.8106(8); Ru(1)−C(1), 2.191(4); Ru(1)−C(2), 2.240(4); Ru(1)−C(3), 2.198(4); Ru(2)−C(1), 2.003(4); Ru(3)−C(3), 2.004(4); C(1)−C(2), 1.408(5); C(2)−C(3), 1.404(5); Ru(2)−Ru(1)−Ru(3), 62.07(2); Ru(1)−Ru(2)−Ru(3), 58.957(15); Ru(1)−Ru(3)−Ru(2), 58.957(15); C(1)−C(2)−C(3), 117.4(3).

η^3:η^1-diruthenaallyl ligand and the μ_3-methylidyne ligand on each face of the Ru_3 triangle.[1011] Since the diruthenaallyl fragment contains a methyl group, the C−C bond scission of the ruthenacyclopentadiene fragment of **4a** should take place at the CH−CH bond rather than the CH−CMe bond. This preference most likely arose from steric reasons, and it is consistent with the slow reaction rate of the thermolysis of **4b** in comparison to that of **4a**.

It is obvious that the C−C bond of the C_4 fragment was cleaved during the step from **4** to **5**. In addition to this, C−C bond cleavage also took place in the formation of **4**. We have recently elucidated the reaction mechanism of the *nido* to *nido* isomerization of **6** into **3a** on the basis of the kinetic studies and the DFT calculations (path A in Scheme 1); the isomerization proceeds via the formation of a μ-methyle-μ_3-diruthenaallyl intermediate formed as a result of C−C bond cleavage of the C_4 moiety of **6**.[11] At lower temperature, C−C bond reformation occurred only at the same side of the Ru_3 plane. In contrast to this, *closo*-type complex **4** was obtained at higher temperature. This was most likely due to flipping of the μ-methylene group of the intermediate toward the opposite side of the Ru_3 plane. It

Scheme 1



seems to be a rational idea that **4** was formed via the same intermediate of the *nido* to *nido* isomerization. After the flipping, the C−C bond would be formed across the Ru_3 plane to afford a *closo*-type complex **4**.

This sequential transformation is a rare example of the skeletal rearrangement of the hydrocarbyls concomitant with the partial breaking and re-formation of the Ru−Ru bond. During the rearrangement of the C_4 fragment of **3** to **4** and **5**, we have shown the cooperative action of the adjacent metal centers in each step. Such a flexible Ru_3 skeleton indicates the importance of an M−M bond for the multimetallic activation, in this case C−C bond cleavage.

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Supporting Information Available: Text, tables, and figures giving synthetic details for compounds **4a**, **4b**, **5a**, and **5b**, and X-ray crystallographic files of **4b** and **5a**; 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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(10) Crystal data for **5a**: $C_{35}H_{52}Ru_3$, fw = 775.98, monoclinic, space group $P2_1/c$, a = 10.949(4) Å, b = 17.795(4) Å, c = 17.362(4) Å, β = 107.795(17)°, V = 3221.1(15) Å^3, Z = 4, D_{calcd} = 1.600 g/cm^3, temp −20 °C, μ(Mo Kα) = 14.10 cm^{-1}, R1 = 0.0311, wR2 = 0.0738 for 5413 reflections with $I > 2\sigma(I)$.

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