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Communications

Oxidation-Induced Rearrangement from a *nido*- to a *closo*-Ruthenacyclopentadiene

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*Summary: Two-electron oxidation of a triruthenium nido-ruthenacyclopentadiene complex, {Cp*Ru(μ-H)}$_3$(CMe═CR−CH═CH) (**1a**; R = H, **1b**; R = Me, Cp* = η^5-C$_5$Me$_5$), proceeds at −78 °C and exclusively affords a cationic closo-ruthenacyclopentadiene complex, [(Cp*Ru)$_2$\{Cp*Ru(CH═CMe−CR═CH)\}(μ-H)$_2$](PF$_6$) (**6a**; R = H, **6b**; R = Me).*

Reactivities of complexes that contain a metallacyclopentadiene skeleton have been intensively investigated because they are key intermediates of various catalytic reactions such as cyclotrimerization of alkynes.[1] In this regard, many trimetallic complexes containing a metallacyclopentadiene moiety have been synthesized. As far as triruthenium complexes are concerned, they are classified into two classes, *nido*- and *closo*-ruthenacyclopentadiene complexes. Most of the ruthenacyclopentadiene complexes are *closo*-type (pseudo-pentagonal-bipyramidal structure), in which a ruthenacyclopentadiene moiety bisects one of the Ru−Ru vectors of the trimetallic core.[2]

Previously, we have synthesized another type of metallacyclopentadiene, namely, *nido*-ruthenacyclopentadiene complex, {Cp*Ru(μ-H)}$_3$(μ$_3$-η^2:η^2-CMe═CR−CH═CH) (**1a**; R = H, **1b**; R = Me, Cp* = η^5-C$_5$Me$_5$).[3] In contrast to abundant examples of the *closo*-metallacyclopentadiene complexes, the *nido*-type is still rare.[4]

We have demonstrated the skeletal rearrangement of the *nido*-**1** to *closo*-ruthenacyclopentadiene complex **4** by way of *nido*-**2** (Scheme 1).[5] The *nido* to *nido* isomerization was rationalized by a sequence of reactions, namely, C−C bond cleavage to form a μ$_3$-diruthenaallyl-μ-methylene intermediate **3** and re-formation of the C−C bond at the opposite end of the allylic moiety.[5a] Transformation to the *closo*-type complex **4**

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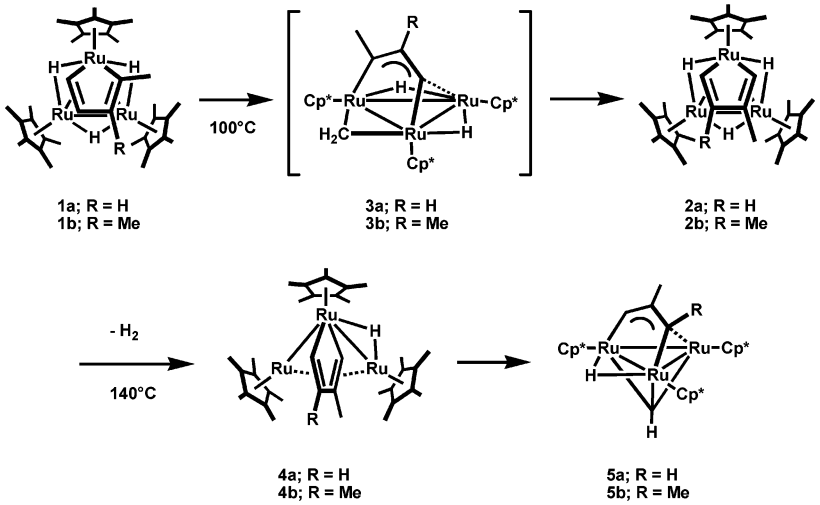
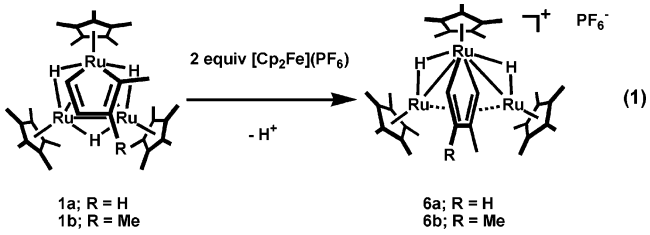
Scheme 1



would proceed via an intermediate similar to **3** and would involve flipping of the μ-methylene ligand to the opposite face of the Ru_3 plane.[5b]

In this communication, we report a novel type of skeletal rearrangement of the *nido*-ruthenacyclopentadiene induced by chemical oxidation. We have already reported skeletal rearrangements of a hydrocarbyl ligand on the Ru_3 core induced by oxidation.[6] Two-electron oxidation of a μ_3-diruthenaallyl complex, $(Cp^*Ru)_3(H)_4(\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-CMeCHCH})$, resulted in C−C bond formation to yield a tris(μ-alkylidene) complex, $[\{Cp^*Ru(\mu\text{-H})\}_3(\mu_3\text{-}\eta^3\text{-}C_3MeH)]^+$, which contains a C_3 ring on the Ru_3 plane.[6b] In contrast, oxidation of *nido*-**1** did not yield a C_4 ring but a cationic *closo*-ruthenacyclopentadiene complex, **6**, exclusively.

Treatment of **1** with 2 equiv of $[Cp_2Fe](PF_6)$ (Fc^+; Cp = η^5-C_5H_5) in toluene immediately afforded a cationic *closo*-ruthenacyclopentadiene complex, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^4\text{:}\eta^4\text{-CH=CMe−CR=CH−})\}(\mu\text{-H})_2](PF_6)$ (**6a**; R = H, **6b**; R = Me) as a red precipitate (eq 1).[7] Oxidation of **1** was complete at −78 °C within 2 h. Oxidation of **1** did not afford any byproducts containing a μ_3-methylidyne group, while thermolysis of **1** at 140 °C was accompanied by further skeletal rearrangement of **4**, namely, formation of μ_3-methylidyne-μ_3-diruthenaallyl complex **5**.



(1)

A red single crystal of **6a** suitable for an X-ray diffraction study was obtained from a cold THF solution.[8] The diffraction study clearly demonstrates the open-form *closo*-structure of **6a**. The structure of the cationic part of **6a** is depicted in Figure 1 along with relevant bond lengths and angles.

The Ru−Ru bond lengths of **6a** (ca. 2.76 Å) are slightly shorter than those of the neutral *closo*-ruthenacyclopentadiene complexes, **4b**[5b] and $(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}\eta^4\text{:}\eta^4\text{-CEt=CH−CH=CH-})\}(\mu\text{-H})$ (**7**)[9] (av 2.79 Å), but these values still lie in the range of an Ru−Ru single bond length. Direct bonding interaction between the Ru(2) and the Ru(3) (Ru(2)···Ru(3), 3.72 Å) was negligible, as reported in other *closo*-ruthenacyclopentadiene complexes.[2]

The metal-bound hydrogen atoms, H(20) and H(30), were located during the differential Fourier synthesis. Interestingly, addition of a proton to the neutral *closo*-ruthenacyclopentadiene complex had little influence on the structural parameters. The Ru(2)−Ru(1)−Ru(3) angle (84.57(2)°) is nearly equal to those of the neutral ones (**4b**, 83.974(12)°;[5b] **7**, 83.72(3)°[9])

The ruthenacyclopentadiene moiety is approximately planar (sum of the interior angles is 540.1°), and a similarity among the C−C bond lengths (C(1)−C(2), 1.440(8) Å; C(2)−C(3), 1.467(7) Å, C(3)−C(4), 1.449(7) Å) shows that π-electrons are delocalized over the ruthenacyclopentadiene moiety. This type

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(7) Toluene (10 mL) and a *nido*-2-methylruthenacyclopentadiene complex, $\{Cp^*Ru(\mu\text{-H})\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-CMe=CH−CH=}\mathit{CH}\text{−})$ (**1a**; 93.6 mg, 0.120 mmol), were charged in a 50 mL reaction flask. After $[Cp_2Fe](PF_6)$ (80.1 mg, 0.242 mmol) was added to the solution at room temperature, the solution was vigorously stirred for 2 h. The color of the solution immediately turned from purple to yellow, and a red precipitate was formed. The precipitate was separated by removing the supernatant, including ferrocene, and rinsed three times with 5 mL of pentane. The precipitate was then dissolved in 10 mL of CH_2Cl_2 and rinsed with 15 mL of water three times by the use of a separatory funnel in order to remove remaining $[Cp_2Fe](PF_6)$ and liberated acid. After the organic layer was dried over Na_2SO_4 followed by filtration, the solvent was removed under reduced pressure. A 87.5 mg amount of **6a** was obtained as a red solid (79.4 % yield). Complex **6b** was synthesized in 90.0 % yield in a similar way using **1b** as a starting material. **6a**: ^{1}H NMR (400 MHz, THF-d_8, 23 °C) δ 5.52 (d, J_{HH} = 4.8 Hz, 1H, $C^3\mathit{H}$), 3.41 (s, 1H, $C^1\mathit{H}$), 3.23 (d, J_{HH} = 4.8 Hz, 1H, $C^4\mathit{H}$), 2.63 (s, 3H, $-C^2C\mathit{H}_3$), 2.11 (s, 15H, $C_5\mathit{Me}_5$), 1.89 (s, 30H, $C_5\mathit{Me}_5$), −8.11 (s, 2H, Ru-*H*); ^{13}C NMR (100 MHz, THF-d_8, 23.0 °C) δ 114.1 (d, J_{CH} = 159.6 Hz, $-C^1$H), 108.1 (d, J_{CH} = 158.6 Hz, $-C^4$H), 96.8 (s, C_5Me$_5$), 92.9 (s, C_5Me$_5$), 79.7 (s, $-C^2CH_3$), 72.0 (d, J_{C-H} = 152.4 Hz, $-C^3$H), 20.2 (q, J_{C-H} = 126.7, $-C^2CH_3$), 13.1 (q, J_{C-H} = 126.2 Hz, $C_5\mathit{Me}_5$), 12.3 (q, J_{C-H} = 127.0 Hz, $C_5\mathit{Me}_5$). **6b**: ^{1}H NMR (400 MHz, acetone-d_6, 23 °C) δ 3.51 (s, 2H, $C^1\mathit{H}$ and $C^4\mathit{H}$), 2.89 (s, 6H, $-C^2C\mathit{H}_3$ and $-C^3C\mathit{H}_3$), 2.14 (s, 15H, $C_5\mathit{Me}_5$), 1.87 (s, 30H, $C_5\mathit{Me}_5$), −7.92 (s, 2H, Ru-*H*); ^{13}C NMR (100 MHz, acetone-d_6, 23 °C) δ 112.9 (d, J_{C-H} = 163.6 Hz, $-C^1$H and $-C^4$H), 95.6 (s, C_5Me$_5$), 91.6 (s, C_5Me$_5$), 77.3 (s, $-C^2CH_3$ and $-C^3CH_3$), 19.1 (q, J_{C-H} = 127.0 Hz, $-C^2\mathit{C}H_3$ and $-C^3\mathit{C}H_3$), 11.8 (q, J_{C-H} = 126.7 Hz, $C_5\mathit{Me}_5$), 10.9 (q, J_{C-H} = 126.7 Hz, $C_5\mathit{Me}_5$).

(8) Crystal data for **6a**: $C_{35}H_{53}F_6PRu_3$, fw = 921.95, monoclinic, space group $P2_1/n$ (#14), a = 15.180(5) Å, b = 15.044(8) Å, c = 17.907(6) Å, β = 94.82(3)°, V = 4075(3) Å^3, Z = 4, D_{calcd} = 1.503 g/cm^3, temp −50 °C, μ(Mo Kα) = 11.85 cm^{-1}, R_1 = 0.052, wR_2 = 0.149 for 6753 reflections with $I > 2\sigma(I)$. Hydrogen atoms attached to the ruthenium atoms were located by sequential difference Fourier synthesis and refined isotropically.

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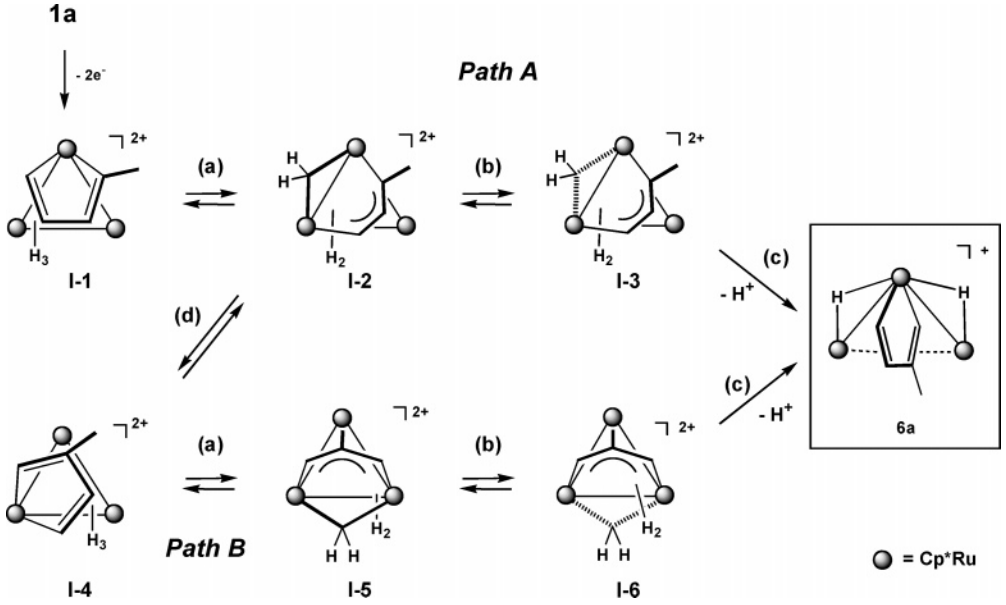
Scheme 2[a]



[a] (a) C−C bond cleavage. (b) Flipping of the μ-methylene group across the Ru_3 plane. (c) C−C bond formation across the Ru_3 plane. (d) C−C bond formation on the same side of the Ru_3 plane.

of delocalization is observed for the other *closo*-ruthenacyclopentadiene complexes, and the C−C bond lengths of **6a** lie within the reported range (1.42−1.48 Å).[2]

Two signals stemming from the Cp* groups of **6a** appeared at δ 1.89 and 2.11 with the intensity ratio of 2:1. The methine protons at C(1) and C(4) were observed at δ 3.41 (s) and 3.23 (d, J_{HH} = 4.8 Hz), respectively. These appeared in higher magnetic field than those of **4a** (δ 4.34 and 4.18)[5b] by ca. 0.9 ppm. In contrast, the methine signal at the C(3) shifted downfield (δ 5.52, d, J_{HH} = 4.8 Hz) by 0.9 ppm in comparison to that of **4a**. A similar trend was also seen in the ^{13}C NMR spectrum, i.e., an upfield shift for the signals for C(1) and C(4) and a downfield shift for those of C(2) and C(3) in comparison with those of neutral **4a**.

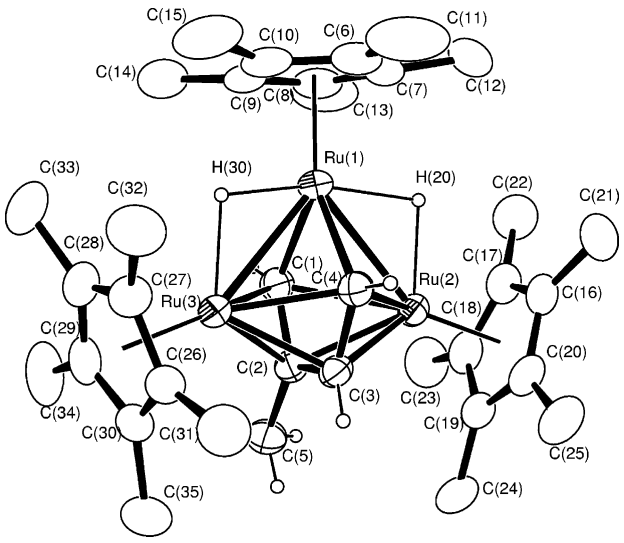


Figure 1. Molecular structure and labeling scheme of the cationic part of **6a** with thermal ellipsoids at the 30% probability level. The anionic part is omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2), 2.7612(10); Ru(1)−Ru(3), 2.7669(10); Ru(1)−C(1), 2.074(5); Ru(1)−C(4), 2.122(6); C(1)−C(2), 1.440(8); C(2)−C(3), 1.467(7), C(3)−C(4), 1.449(7); Ru(2)−Ru(1)−Ru(3), 84.57(2); C(1)−Ru(1)−C(4), 75.8(2); Ru(1)−C(1)−C(2), 121.2(4); C(1)−C(2)−C(3), 111.5(4); C(2)−C(3)−C(4), 113.7(5); Ru(1)−C(4)−C(3), 117.9(4).

Although complex **6a** was monocationic, 2 equiv of Fc^+ was essential to complete the reaction. In order to elucidate the reaction mechanism, a THF solution of **1a** was subjected to CV scan. In the cyclic voltammogram of **1a**, quasi-reversible ($E_{1/2}$ = −319 mV) and irreversible one-electron waves (E_{pa} = +60 mV) were observed. Two-electron oxidation would, therefore, be performed by the use of Fc^+ ($E°$ = 159 mV vs Ag/Ag^+), and thus **6a** would be formed as a consequence of oxidation and subsequent skeletal rearrangement followed by deprotonation. The cyclic voltammogram of **1a** closely resembles that of the μ_3-diruthenaallyl complex, $(Cp*Ru)_3(H)_4(\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-CMeCHCH})$, which is converted to a monocationic tris(μ-carbene) complex, $[\{Cp*Ru(\mu\text{-H})\}_3(\mu_3\text{-}\eta^3\text{-}C_3MeH)]^+$, via two-electron oxidation and subsequent deprotonation.[6b]

We previously reported a thermal rearrangement of the *nido*-ruthenacyclopentadiene complex **1** to *closo*-**4** and proposed a reaction mechanism based on the DFT calculation, which involved formation of a μ_3-diruthenaallyl-μ-methylene intermediate.[5a] As found in the thermal skeletal rearrangement of **1**, the methyl group on the ruthenacyclopentadiene moiety migrates from the 2- to the 3-position of the metallacycle. This implies that formation of **6a** proceeded in a similar manner to the thermal skeletal rearrangement. According to the precedent, the most plausible reaction paths from **1a** to **6a** are represented in Scheme 2.

Two-electron oxidation of **1a** affords a dicationic intermediate **I-1**. Due to the cationic charge on the metal centers, the hydrides should become acidic. The increase in acidity of the hydrido ligand would be responsible for acceleration of the hydride migration to the electron-rich carbon atom directly bound to the ruthenium atom. Migration of a hydrido ligand to the hydrocarbyl moiety lowers the bond order of the C−C bond, which results in C−C bond cleavage to form **I-2**. A similar bond-breaking reaction by the assistance of the hydride migration was observed in the C≡N bond cleavage of the coordinated nitrile ligand on a triruthenium center.[10]

There are two possible routes from **I-2** to **6a**; path B involves preisomerization to *nido*-ruthenacyclopentadiene complex **I-4**,

while path A does not involve the *nido* to *nido* isomerization. At present, it is not clear whether the skeletal rearrangement proceeds via path A or B.

Flipping of the μ-methylene group in **I-2** (or **I-5**) across the Ru_3 plane to form **I-3** (or **I-6**) and subsequent C−C bond formation followed by deprotonation would afford **6a**. Flipping of the μ-methylene ligand from the top of the Ru_3 face to the bottom within the NMR time scale has been reported for $Ru_3(\mu\text{-}CH_2)(CO)_8\{\mu\text{-}N(R)=C-C=NR\}$.[11]

Thus, skeletal rearrangement of the *nido*-ruthenacyclopentadiene to the *closo*-structure was effectively accelerated by the oxidation. While similar skeletal rearrangement occurred upon thermolysis at 140 °C, transformation to the *closo*-structure by oxidation can proceed even at −78 °C. Such smooth rearrangement induced by oxidation can be explained as follows: oxidation increases the acidity of a hydrido ligand, which causes acceleration of the intramolecular migration of the hydrido ligand to the electron-rich carbon atom. This hydride migration induces rearrangement of the hydrocarbyl ligands. This result implies that the acidity of the hydrido ligand strongly affects the reactivity of a polyhydrido cluster. We are currently investigating protonation, which also brings about rapid skeletal rearrangement of a hydrocarbyl moiety on the Ru_3 plane, in order to prove the role of the hydrido ligand.

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Supporting Information Available: Text, tables, and figures giving synthetic details for compounds **6a** and **6b**, and X-ray crystallographic files of **6a**; the 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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