Cluster Compounds

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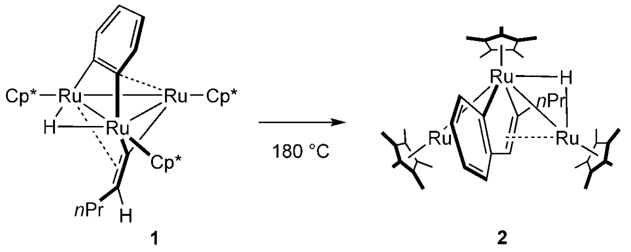
Metathesis Reaction of Hydrocarbyl Ligands across the Triruthenium Plane**

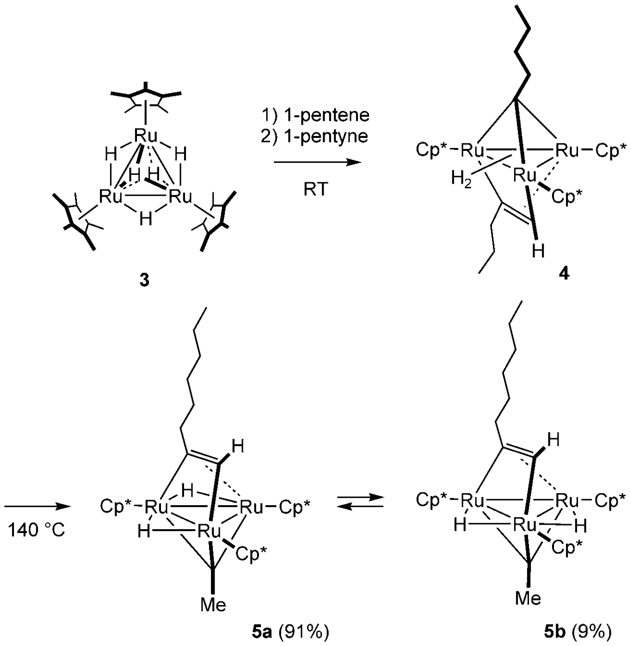
*Atsushi Tahara, Mana Kajigaya, Makoto Moriya, Toshiro Takao, and Hiroharu Suzuki**



Scheme 1. C–C bond formation in a trimetallic cluster accompanied by M–M bond breaking. Cp* = pentamethylcyclopentadienyl.

Carbon-chain recombination, similar to that observed during the cracking of alkanes and in the Shell higher olefin process, is one of the most important reactions in the chemical industry. There has been a continuous demand for a process that can yield hydrocarbons of desired chain length. Recently, a method for converting lower alkanes into higher alkanes, which is referred to as alkane metathesis, has been reported.[1] Alkane metathesis has considerable scientific and industrial importance because it can convert gaseous hydrocarbons into liquid fuels. Such interconversion involves three catalytic reactions: activation of the alkane C–H bond, olefin metathesis, and hydrogenation of the formed olefins. However, because of the cross-metathesis of the alkenes during the recombination process, the product will have a molecular weight distribution to some extent.

Coupling reactions between two hydrocarbyl ligands placed on both faces of a trimetallic plane have often been seen in organometallic chemistry,[2] as has C–C bond scission on a cluster.[3] These reactions have attracted considerable attention and are considered to be characteristic of cluster compounds. We have studied C–C bond formation on a triruthenium cluster by directing our attention to the roles of an M–M bond.[4] Recently, we reported the synthesis of **2** using the coupling reaction of μ_3-benzyne and μ_3-vinylidene ligands separated by the Ru_3 plane of **1** (Scheme 1).[4c] In this reaction, the formation of the ruthenacyclopentadiene skeleton was accompanied by the rupture of a Ru–Ru bond. We also reported the scission of a C–C bond in a ruthenacyclopentadiene skeleton in which a Ru_3 triangle was reconstructed.[4a] Such flexibility in a cluster skeleton would enable a novel recombination of hydrocarbons. Herein, we report an unprecedented selective interconversion of two C_5 fragments into C_8 and C_2 fragments on a triruthenium cluster.



Scheme 2. Preparation of an equilibrated mixture of **4**, and its thermolysis to yield an equilibrated mixture of **5a** and **5b**.

The thermolysis of **4**, which was obtained by the sequential treatment of **3** with 1-pentene and 1-pentyne,[5] resulted in the quantitative formation of an equilibrated mixture of **5a** and **5b** (Scheme 2). At ambient temperature, the motion of the hydrido ligand was so rapid that the signals of **5a** and **5b** coalesced. For simplification, we denote this equilibrated mixture as **5**.[6] The structures of **4** and **5** were determined by X-ray diffraction studies (Figure 1 and Figure 2, respectively).[7] These results clearly indicate that the μ_3-pentylidyne and μ_3-pentyne ligands in **4** were respectively transformed into the μ_3-ethylidyne and μ_3-octyne ligands in **5**.

This rearrangement required the migration of the C_3 fragment across the Ru_3 plane. In order to elucidate the mechanism, we monitored the reaction by means of NMR spectroscopy. Upon heating at 80 °C, formation of the μ_3-butylidyne-μ_3-hexyne complex **6** was observed (Path a in Scheme 3). For the formation of **6**, a carbyne group must

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[*] A. Tahara, M. Kajigaya, Dr. M. Moriya, Dr. T. Takao, Prof. H. Suzuki
Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology
O-okayama, Meguro-ku, Tokyo 152-8552 (Japan)
Fax: (+81) 3-5734-3913
E-mail: hiroharu@n.cc.titech.ac.jp

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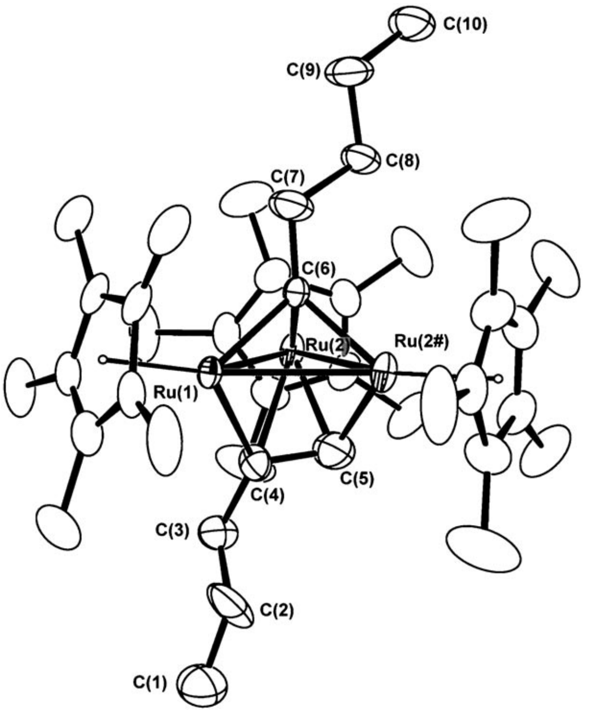


Figure 1. Molecular structure of **4** with thermal ellipsoids set at 30% probability. Disordered atoms were omitted for clarity.

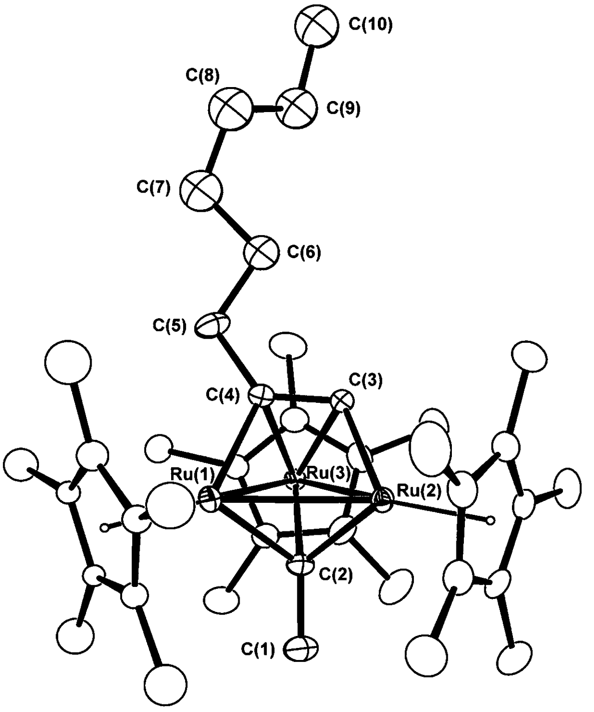
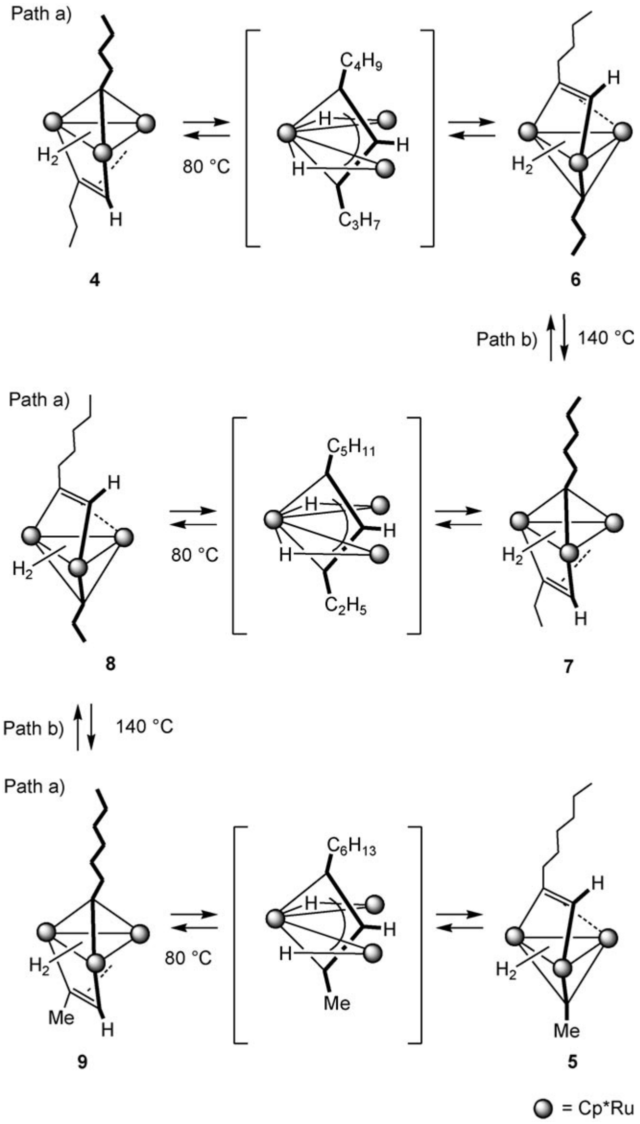


Figure 2. Molecular structure of **5** with thermal ellipsoids set at 30% probability. Disordered atoms were omitted for clarity.

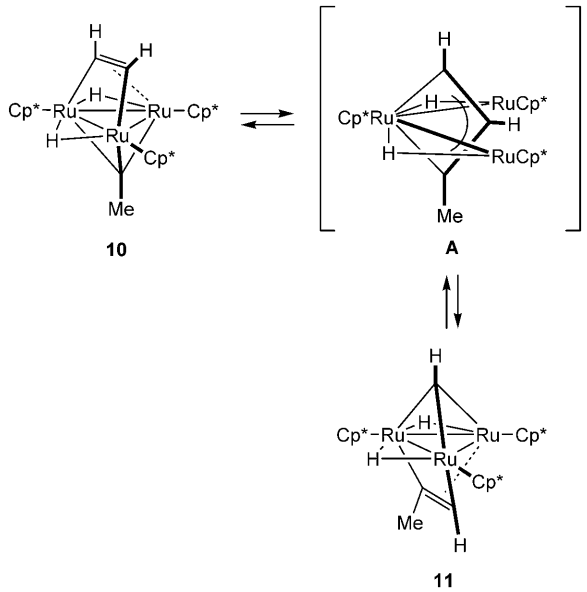
migrate from the μ$_3$-pentyne ligand to the opposite face and connect with the μ$_3$-alkylidyne carbon to form a μ$_3$-hexyne ligand.

The **4**/**6** ratio reached 52:48 within 1 hour. It was anticipated that **4** would equilibrate with **6**, but selective irradiation of the signal derived from **4** was inhibited by the close appearance of the signals derived from **6**. Instead, spin-saturation-transfer was clearly observed for a similar equilibrated mixture obtained from μ$_3$-ethylidyne-μ$_3$-ethyne complex **10** (Scheme 4).[8] Complex **10** equilibrates with the μ$_3$-methylidyne-μ$_3$-propyne complex **11** at 100 °C.[9] Irradiation of the methine signal of **10** ($\delta = 7.25$ ppm) at 80 °C resulted in complete disappearance of the methylidyne signal in **11** at $\delta = 14.35$ ppm. These results clearly indicate that the methylidyne ligand of **11** was formed by scission of the C−C bond of the μ$_3$-ethyne ligand in **10**. The subsequent migration of the rest of the carbyne group and its connection with the μ$_3$-ethylidyne group afforded the μ$_3$-propyne ligand.



Scheme 3. A plausible mechanism for the consecutive recombination of hydrocarbyl ligands on the Ru$_3$ cluster.

It is surprising that such a complicated rearrangement involving alternate coupling and decoupling of the carbyne fragment across the trimetallic plane proceeds within a relatively short timescale. This observation can be rational-



Scheme 4. Equilibrium between **10** and **11** through reversible Ru–Ru bond cleavage.

ized only by considering the reversible partial-breaking of the cluster skeleton (Scheme 4). As seen in the formation of **2**, a C–C bond would be formed with a breaking of one of the Ru–Ru bonds, which would yield the μ_3-ruthenacyclobutenyl intermediate **A**. Subsequent reformation of the Ru–Ru bond concomitant with C–C bond cleavage at the adjacent position would furnish the carbyne migration. An "edge-mechanism", which involves the rearrangement of an alkyne ligand from a μ_3-position to a μ-position on an M–M edge, has previously been proposed as a mechanism for the carbyne migration on the basis of extended Hückel calculations.[3a] A mechanism involving reversible cleavage of an M–M bond in a trimetallic skeleton appears to be taken into account in some cases.

When a mixture of **4** and **6** was heated at 140 °C, a pair of new peaks appeared next to the signals of **4** and **6** (see the Supporting Information). These two peaks could be assigned to signals derived from the μ_3-hexylidyne-μ_3-butyne complex **7** and the μ_3-propylidyne-μ_3-heptyne complex **8**, respectively. Their characterization was carried out by comparison of their spectra with those of authentic samples of **7**, which was independently prepared by sequential treatment of **3** with 1-hexene and 1-butyne, and **8**, which was obtained in a similar manner by using propene and 1-heptyne.

During the isomerization from **4** into **5**, the individual hydrocarbyl ligands undergo skeletal rearrangement on each face of the Ru_3 plane. The μ_3-butylidyne ligand was converted into the μ_3-butyne ligand, and the μ_3-hexyne ligand was converted into the μ_3-hexylidyne ligand (Path b in Scheme 3). Although there have been many reports of the conversion of a μ_3-alkyne ligand into a μ_3-alkylidyne ligand on a trimetallic hydrido cluster in regards to the hydrogenation of alkyne,[10] its reverse reaction has been hardly observed. However, the formation of a μ_3-vinylidene ligand is known to occur.[8,11] Thus, the alkyne ligands are most likely formed through the formation of μ_3-alkenylidene intermediates.

All of the signals derived from the intermediates shown in Scheme 3 diminished upon further heating, and convergence into **5** was achieved within 24 hours. Whereas **9** was not observed during this experiment, it is likely that all of the complexes shown in Scheme 3 exist in equilibrium. The fact that all other species except for **5** diminished suggests that **5** is much more stable than others. The reason why the skeletal rearrangement stopped at **5** is not clear at present; however, we suspect that the energetic barrier for the transformation of a μ_3-ethylidyne ligand into a μ_3-ethyne ligand is so high that the μ_3-ethylidyne ligand is kinetically stabilized.

The series of reactions mentioned here correspond to a selective redistribution of two C_5 molecules into C_2 and C_8 molecules. Such a consecutive carbyne migration is unprecedented, and would only be achieved by using the flexibility of the cluster skeleton showing reversible cleavage of an M–M bond. Although C–C bond formation across a trimetallic plane of a bis(μ_3-alkylidyne) complex has often been observed to yield a ($\perp$)-alkyne complex,[2a–c] such a rearrangement involving the migration of multiple carbon fragments has been quite limited; to the best of our knowledge, there has been only one example, in which migration of a C_2 fragment was shown by using a double-deck Co_3 system.[12] However, there was simultaneous degradation of the cluster skeleton due to high temperature, and mechanical insights in this rearrangement were not clearly shown.

In summary, we have succeeded in a selective recombination of two C_5 molecules into C_2 and C_8 fragments on a triruthenium cluster. The key-step of this transformation is presumably the formation of a μ_3-metallacyclobutenyl intermediate with cleavage of an M–M bond. These results demonstrate the potential usefulness of cluster compounds in synthetic reactions. They may also shed light on the mechanism of complicated reactions on metal surfaces, particularly of those performed on defects, such as steps and kinks.

Experimental Section

All air- and moisture-sensitive compounds were manipulated using standard Schlenk and high-vacuum line techniques under an argon atmosphere. Dehydrated toluene and pentane were purchased from Kanto Chemicals and stored under an argon atmosphere. [D$_8$]toluene and [D$_8$]tetrahydrofuran were distilled from sodium benzophenone ketyl and stored under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer. ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard. ^{13}C NMR spectra were referenced to the natural-abundance carbon signal of the solvent employed. Elemental analysis was performed on a Perkin–Elmer 2400II series CHN analyzer. Experimental details for the synthesis of **4**, **5**, **7**, and **8**, and results of the crystallographic studies are given in the Supporting Information.

Synthesis of **5**: Toluene (10 mL) and **4** (52.3 mg, 0.065 mmol) were placed in a glass-tube equipped with a Teflon valve. The solution was heated at 140 °C for 3 days. The color of the solution did not change from dark-orange over this period. The solvent was then removed under reduced pressure. The resulting solid was extracted with pentane (4 × 5 mL) and filtered on celite. Removal of the solvent under reduced pressure afforded **5** as a brown solid (45.9 mg, 88 % yield). The **5a**/**5b** ratio was estimated to be 91:9 at −40 °C by ^{1}H NMR spectroscopy. **5a**: ^{1}H NMR (400 MHZ, [D$_8$]toluene, −40 °C): $\delta =$

−21.80 (d, ^2J(H,H) = 2.8 Hz, 1 H; RuH), −17.83 (d, ^2J(H,H) = 2.8 Hz, 1 H, RuH), 0.99 (t, ^3J(H,H) = 6.8 Hz, 3 H, CH_3), 1.4–1.6 (m, 6 H, CH_2), 1.70 (s, 15 H, C_5Me_5), 1.77 (s, 15 H, C_5Me_5), 1.78 (m, 2 H, CH_2), 1.88 (s, 15 H, C_5Me_5), 1.92 (m, 1 H, CHHC$_5$H$_{11}$), 2.15 (m, 1 H, CHHC$_5$H$_{11}$), 3.38 (s, 3 H, μ_3-CCH_3), 8.17 ppm (s, 1 H, HC≡CC$_6$H$_{13}$). **5b**: ^{1}H NMR (400 MHz, [D$_8$]toluene, −40 °C): $\delta = -22.22$ (d, ^2J(H,H) = 2.8 Hz, 1 H, RuH), −17.62 (m, 1 H, RuH), 5.70 ppm (d, ^3J(H,H) = 4.0 Hz, 1 H, HC≡CC$_6$H$_{13}$). Other signals derived from **5b** were obscured by the signals derived from **5a**. $C_{40}H_{64}Ru_3$ (848.15): calcd C, 56.64; H, 7.61. found: C 56.77, H 7.75.

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[6] Although the hydrido ligands could not be located owing to a disordered structure about the octyne ligand, their positions were determined, as shown in Scheme 2, on the basis of NMR data measured at −40 °C. Similar behavior was also observed for **4**.

[7] All data were collected on a Rigaku R-Axis RAPID imaging plate Diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at 173 K. Crystal data for **4**: space group *Pnma* (No. 62), $a = 14.9606(5)$, $b = 16.5707(5)$, $c = 15.3695(6)$ Å, $V = 3810.2(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.478\ \mathrm{Mg\,m^{-3}}$, $\mu(Mo_{K\alpha}) = 1.199\ \mathrm{mm^{-1}}$. Of the 42503 reflections that were collected, 3906 were unique ($R_{int} = 0.0512$), $R_1 = 0.0499$ [$I > 2\sigma(I)$], $wR_2 = 0.1324$ [$I > 2\sigma(I)$]. Crystal data for **5**: space group $P\bar{1}$ (No. 2), $a = 11.1146(4)$, $b = 11.2405(4)$, $c = 16.1205(7)$ Å, $\alpha = 71.8400(13)$, $\beta = 82.5810(15)$, $\gamma = 81.2420(10)$°, $V = 1884.20(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.495\ \mathrm{Mg\,m^{-3}}$, $\mu(Mo_{K\alpha}) = 1.212\ \mathrm{mm^{-1}}$. Of the 14339 reflections that were collected, 6874 were unique ($R_{int} = 0.0194$), $R_1 = 0.0377$ [$I > 2\sigma(I)$], $wR_2 = 0.0984$ [$I > 2\sigma(I)$]. CCDC 772021 (**4**) and CCDC 772022 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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